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EXPERIMENTAL RESEARCHES

ON THE

CONSTITUTION

OF

HYDRAULIC MORTARS

BY

HENRI LE CHATELIER

TRANSLATED FROM THE ORIGINAL

BY

JOSEPH LATHROP MACK

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AUTHOR'S PREFACE TO THE ENGLISH EDITION.

My thesis for the degree of Doctor of Science, upon the *Experimental Study of the Constitution of Hydraulic Mortars*, has been, for fifteen years, the starting point of numerous studies; some of these, and especially those of Mr. Newberry, have notably confirmed my first results in regard to the action of supersaturated solutions; to the composition of the calcium silicate, which is the active element in cements; and to its manner of reacting in contact with water. These have been completed in other points, as by the studies of M. Candlot, to whom is due the discovery of two extremely important compounds which relate to the behavior of cements in the sea; the calcium chloro— and sulpho-aluminates. Lastly, my results have been corrected in certain points of detail, as, for example, the formula for hydrated calcium aluminate.

When Mr. J. L. Mack offered to translate my memoir into English, I hesitated a little before accepting. Do studies so old as these possess still sufficient interest to merit reprinting? It would have been necessary to completely recast this work in order to incorporate into it the most recent researches. But I have not the time to do this, and I have taken a middle course. I have indicated in notes the most important advances in our theoretical knowledge of cements and have given the references to the papers in which these studies are recorded.

I apologize for allowing so incomplete a work to be reprinted and I thank Mr. Mack for wishing to take the trouble to translate it. It is nevertheless a great satisfaction to me to think that in a country where such great advances have been realized in the cement industry, my researches still seem to have interest.

H. Le Chatelier.

Villers sur mer, August 1, 1903.

TRANSLATOR'S PREFACE.

Although this thesis of Monsieur Le Chatelier appeared in 1887, it was ten years before any new work of importance was published on the subject of the *Constitution* of Cements. In 1897 the matter again received attention, and the discussion and investigations started at that time have continued up to the present time, and have amplified and confirmed the results obtained by Monsieur Le Chatelier. His classic work therefore stands to-day as the first, the most complete and beautiful piece of work done upon the chemistry of Portland cement, and since the original is not easily obtained and all later work on this subject goes back to and rests upon this thesis, I have thought that it ought to be available to all who are interested in the manufacture and use of Portland cement.

In representing the chemical formulas, the rational form used by the author has been retained because of certain advantages which it possesses over the empirical form, although in some cases the latter might be preferable. But it has been necessary to change some of the formulas slightly to make them conform to the atomic weights which are at present used, for example, "HO" becomes H_2O and "CaCl" becomes $CaCl_2$.

In an appendix has been added some formulas for converting metric into English units. The table which appears on page 122 has been calculated into percentages.

The author has very kindly read the corrected proof, and it is a pleasure to record my appreciation of the kindness and interest shown by him and others during the progress of the translation. Nor should I fail to mention the courtesy and patience of the publishers during preparation of this book.

J. L. M.

FORDWICK, January, 1905.

CONTENTS.

INTRODUCTION.

The chief object of this work is the study of the chemical reactions which are produced in the limes and hydraulic cements, either during their calcination or during their hardening. Having found in these researches difficulties, the existence of which I had not at first suspected, I decided to take up first of all the study of more simple analogous bodies: i.e. *plaster,* then the *silicates of barium,* hoping that by understanding the phenomena found in these bodies, some light would be thrown upon the theory of calcareous cements.

This work, therefore, includes three parts:

Part I.—Plaster.

Part II.—The Silicates of Barium.

Part III.—Cements and Hydraulic Limes.

PART I.

PLASTER.

Historical.—The scientific study of the phenomena which accompany the calcination and hardening of plaster is due to Lavoisier. The details of his experiments are recorded in an extremely remarkable memoir for the time in which it appeared. Chemistry did not yet exist; its most important laws, that of definite proportions among others, had not even been suspected. But the young savant, then only twenty-one years of age, already possessed the experimental method which he was destined to apply to all of his researches and from which he must justly be considered as the founder of modern chemistry. He has summed up his experiments in the following passage, a brief note, inserted in the *Comptes rendus de l'Académie des Sciences:**

"If gypsum, which has been deprived of its water of crystallization by means of heat, is again treated with water (to make what is commonly called mortar) it takes it up with avidity, a rapid and irregular crystallization occurs, and the small crystals which are formed are so entangled in each other that a very hard mass results."

He had noted, further, that calcination at too high a temperature deprives plaster of the property of setting; finally he pointed out an important peculiarity in the

* *Comptes rendus*, 17 février, 1765.

calcination of plaster* which had escaped all authors who have studied this question after him. The dehydration of gypsum occurs in two stages: three-fourths of the combined water is much more easily driven out than the last fourth.

Our present knowledge of plaster is limited, or very nearly so, to about the preceding results; it has scarcely been completed by any secondary points.

Berthier† noticed that plaster such as is used in trade contains from 4 to 8 per cent. of water. This fact has since been confirmed by the recent researches of M. Landrin.‡

Payen,§ about 1830, tried to determine the exact temperature of the calcination of plaster. He noticed that gypsum begins to lose its water at about 115° C. and loses it afterwards more and more rapidly in proportion as the temperature rises.

My personal researches have been upon the *calcination* and the *set* of plaster.

Calcination.—The daily experience of the manufacturers of plaster has taught that the calcination of plaster occurs at a low temperature, well below a red heat. From the laboratory experiments due to Payen, complete dehydration will occur between 115°C. and 120° C. However, the figures given by different authors are entirely discordant, and vary from 110° C. to 300° C. It is interesting to take up again this study, which evidently remains incomplete.

I have employed for this purpose the method by progres-

Lavoisier Œuvres Complètes, t. III., p. 122.
Berthier, *Ann. des Mines*, 3e série, t. XIX., p. 655, 1841.
Landrin, *Ann. de phys. et de Chim.*, 5e série, t. III., p. 441.
Payen, *Chimie industrielle*, 1851, p. 304.

sive heating proposed by Regnault to study the allotropic modifications of molten sulphur. Pulverized gypsum was put into a glass tube in the middle of a paraffin bath, the temperature of which was raised in a progressive and very regular manner. A thermometer gave at each instant the temperature of the salt and the passage of the mercury column past each division of the stem was marked by a registering chronograph. The rise in temperature thus determined ought to remain regular unless some unique phenomenon occurred and should present, as it rose, at the moment of dehydration a period of rest in which it slackened, indicating a corresponding absorption of heat, and then should reassume its normal rate of increase. Contrary to this expectation, instead of only slackening once, the rise in temperature has slackened twice, as will be seen from the table below:

LAW OF HEATING OF GYPSUM.

Temperature.	Hours.		Differences.	
C°	min.	sec.	min.	sec.
100		0		0
105		20		20
110		45		25
115	1	20		35
120	2	0		40
125	2	50		50
130	18	0	15	10
135	21	30	3	30
140	23	30	2	0
145	24	40	1	10
150	25	40	1	0
155	26	50	1	0
160	27	50	1	10
165	30	40	2	50
170	31	40	1	0
175	32	40	1	0
180	33	30		50
185	34	15		45
190	34	55		40
195	35	30		35
200	36	0		30

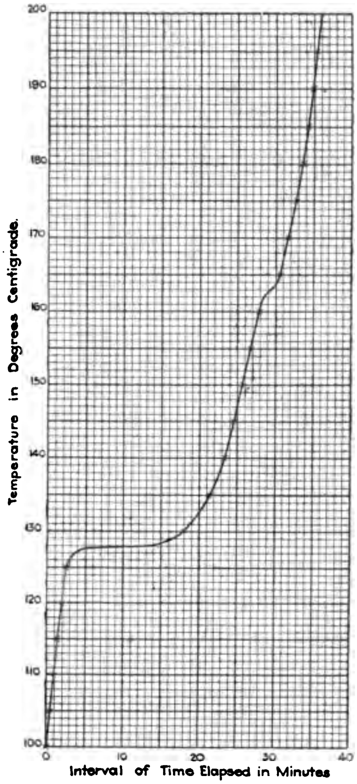

PLATE I. LINE SHOWING RATE OF RISE IN TEMPERATURE OF GYPSUM WHEN THE TEMPERATURE OF THE CONTAINING VESSEL IS RAISED IN A REGULAR AND UNIFORM MANNER.

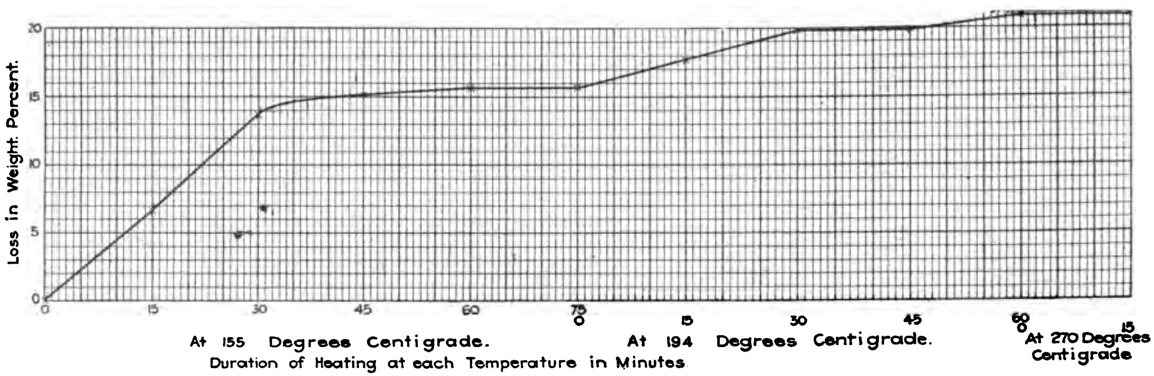

PLATE II, LINE SHOWING RATE OF LOSS OF WEIGHT ON HEATING GYPSUM AT CERTAIN CONSTANT TEMPERATURES

The temperature-curve very plainly shows two halting points, although not equally marked, the first, corresponding to a temperature of 128° C. is evidently produced by the dehydration of the gypsum; the second, corresponding to 163° C., may be attributed either to the end of the dehydration, on the assumption that these phenomena occur in two phases, or to an allotropic modification succeeding the dehydration.

In order to decide this question, I have determined the loss in weight suffered by gypsum when it is heated to a temperature above one of these halting points only, and then above both of them. The experiment was made upon 5 grams of gypsum heated in a paraffin bath maintained at a constant temperature by means of a Schloesing regulator.

Temperature.	Duration of the heating. hours.	min.	Total loss on 5 grams.	Loss percent.
155° C.		0	0.00	0.0
		15	0.33	6.6
		30	0.68	13.6
		45	0.76	15.2
	1	0	0.78	15.6
	1	15	0.78	15.6
194° C.	0	0	0.78	15.6
		15	0.89	17.8
		30	0.99	19.8
	1	0	0.99	19.8
	1	0	1.04	20.8
270° C.	0	0	1.04	20.8
		15	1.04	20.8

This experiment very clearly shows:

First, *the dehydration is incomplete at 155° and that it is complete at 194°*. The quantity of water contained in pure gypsum, $CaSO_4.2H_2O$, is really 20.9 per cent. The two halting points of the temperature-curve correspond, therefore, to two distinct phases in the dehydration.

Second, *the quantity of water liberated during the first*

phase is perfectly definite and corresponds exactly to 1.5 molecules of water. The product obtained may therefore be represented by the formula $CaSO_4 \frac{1}{2} H_2O$ and contains 6.2 per cent. of water.

In this fact we discover the explanation of certain peculiarities which have been previously pointed out.

The halting points in the heating of plaster noticed by Lavoisier result from the higher temperature necessary to drive out the last fourth of the water by hydration.

The presence of a nearly constant quantity of water in calcined plaster is due to the fact that its industrial calcination is generally limited to the first phase. The proportion of 7 per cent. of water found by M. Landrin differs somewhat from the theoretical quantity, which is 6.2 per cent. The motive for this incomplete calcination seems to be entirely a question of economy of fuel, because the plaster when completely calcined sets equally well and has the advantage of solidifying with a larger quantity of water.

It may be asked if the product of the incomplete calcination of plaster is a chemical compound or a simple mixture of anhydrous calcium sulphate and of sulphate with two molecules of water.

Calcined gypsum is an amorphous material which shows no guaranty of homogeneity. It was interesting to prepare this body in the crystallized state. I have obtained this by heating a saturated solution of calcium sulphate in a sealed tube between 135°-150° C. I thus obtained long, regular, exceedingly slender prisms crystallizing in the rhombic system. But the quantity of these crystals obtained in one experiment is very small, by reason of the slight solubility of gypsum. In order to obtain a quantity at all considerable, it is necessary to put an excess of cal-

cium sulphate in the water; the crystallization is then very confused. It is indispensable to separate the crystals rapidly from the water in the midst of which they are formed because below 130° C. they again hydrate rapidly to become gypsum. They are obtained by breaking the warm tube, which causes the instantaneous evaporation of the larger part of the water, and throwing the moist material into absolute alcohol, then draining rapidly and drying them in a drying oven at 100° C. The analysis of these crystals gave me these results:

	Observed.	Calculated.
Water	6.7	6.2
$CaSO_4$ (difference)	93.3	93.8
	100.0	100.0

which shows that the body thus obtained is well represented by the formula

$$CaSO_4.\tfrac{1}{2}H_2O$$

It is the same compound which constitutes the incrustations of boilers using sea water. The following is the result of an analysis of a similar sample coming from the boilers of the steamers of the Transatlantic company:

Analysis.

$CaCo_3$	0.3
Fe_2O_3	2.0
H_2O	5.8
$CaSO_4$ (difference)	91.9
	100.0

This hydrate obtained in the superheated water corresponds to calcined plaster, its temperature of rapid dehydration lies between 160° and 170° C. When finely ground and gauged with water, it hydrates and hardens.

The set, it is true, is less rapid and less complete than with plaster, which is probably due to the greater volume of the product.

It therefore is fully demonstrated that pure, ordinary plaster of good quality, e.g. moulding plaster, is not anhydrous calcium sulphate, as has been admitted hitherto, but a definite hydrate.

$$CaSO_4 . \tfrac{1}{2} H_2O.$$

We know since the experiments of M. Debray upon the saline hydrates that their decomposition is limited to a temperature given by a definite vapor tension and that the different hydrates of the same salt are characterized by different tensions at the same temperature. I have concluded directly from this that the temperatures of decomposition of the two hydrates of calcium sulphate are precisely those for which their vapor tensions were equal to the atmospheric pressure, and that consequently the temperature of decomposition would be lowered by diminishing the pressure. The result has been entirely contrary to this expectation, as the following table shows:

Pressure.	1st temperature stationary.	2d temperature stationary.
760 mm.	128° C.	163° C.
316	128	...
280	...	165°
200	125	164°

The temperature of decomposition is therefore entirely independent of the pressure; the phenomenon observed is not one of dissociation. I have discovered, however, in using the customary methods of experimentation that the dissociation temperature of calcium sulphate with two equivalents of water under the pressure of 760 millimeters is about 110°, that is to say, notably lower than its temperature of rapid decomposition. It is a very tedious

operation to attain uniform pressure, which made precise experiments very difficult and forced me to give up the attempt.*

The speed of decomposition, which is very slow at the normal temperature of dissociation, becomes more and more rapid as the temperature rises, becoming quite instantaneous or at least so rapid that it completely escapes measurement. It is this temperature of rapid decomposition that we observe in the experiments of progressive heating. The preceding experiments show that it is independent of the pressure. I have noticed further that it differs little from that at which gypsum begins to dehydrate in the presence of liquid water.

It can be foreseen that this temperature of decomposition will vary with the rapidity of the heating. I have been able, indeed, to raise it to 133° C. by heating very rapidly the paraffin bath used in the experiments. For the same reason, the temperature of industrial calcination may be a little lower by reason of the greater time required for the heating of the relatively voluminous pieces of plaster stone. Experiments upon one hundred kilograms of material by M. Lacauchie, director of the plaster works at Argenteuil, have given 125° C., a figure scarcely differing from 128° C. which I have found when working on ten grams of gypsum.

It is therefore confirmed that the temperature of the calcination of plaster differs from its temperature of dis-

*This question has been taken up again by Mr. van't Hoff† and completely solved in spite of its great difficulties. The dissociation-temperature of gypsum is still lower than I had supposed and differs little from the vapor tension of water. The salt with half a molecule of water has, contrary to what one might suppose, a greater tension than that of gypsum, and it can only exist in the metastable state.

†*Proceedings of the Academy of Sciences of Berlin, 1900-1901.*

sociation and that it is always higher than the latter, that it is independent of the pressure, that it is not theoretically susceptible of being precisely determined, but that in fact it varies within rather narrow limits, and that it is comprised between 120° and 130° C.

THE SETTING OF PLASTER.—Lavoisier, as I have said above, has shown that plaster during its setting takes up a quantity of water equal to that which had been liberated from it during its calcination, reproducing crystallized gypsum identical to that which constitutes the plaster stone. This analysis of the phenomenon of set is evidently incomplete; it does not show how the hydrate which is produced *crystallizes,* nor how this crystallization leads to the hardening of the entire mass.

In all the special memoirs or treatises of general chemistry which hitherto have considered plaster, the physical phenomenon of crystallization has generally been passed over in silence and the hardening has been attributed, without any explanation, to the massing or felting of the crystals formed. However, we can scarcely understand how rectilinear crystals will be able to become entangled in the manner of twisted fibres which constitute a felt. The bending of these elastic threads gives a reactive force which presses them one against another and causes the development of rubbing stresses at the point of contact. This is the only cause of longitudinal resistance of similar systems. Rigid crystals are unable to cause such phenomena. A very simple experiment will show the insufficiency of this explanation; by precipitating a solution of calcium sulphate by alcohol, a deposit of small crystals of gypsum is obtained, showing as complete a massing as can be wished, but nevertheless possessing no cohesion. I therefore think myself authorized to say that this question

of the physical phenomena of the hardening of plaster has remained entirely untouched up to the moment when I began the study of it. The solution of the problem has a considerable importance because it was quite probable *a priori,* that the setting of all mortars occurs in an analogous manner, and that in each case we can distinguish between:

The chemical phenomenon of hydration,

The physical phenomenon of crystallization, and

The mechanical phenomenon of hardening.

HYDRATION.—Little can be added to what Lavoisier has said about the chemical reaction; gypsum $CaSO_4.2H_2O$ identically the same as the raw stone re-forms. Only since plaster contains already half a molecule of water, it does not fix more than one and one-half molecules in contact with water.

$$CaSO_4.\tfrac{1}{2}\,H_2O + 1\tfrac{1}{2}\,H_2O = CaSO_4.2H_2O$$

THE CRYSTALLIZATION OF PLASTER.—In all the known cases of crystallization of salts in contact with water, the formation of crystals is preceded by the solution of the salt, which gives to the molecules the freedom of motion necessary to allow them to dispose themselves according to a geometrical arrangement. It is therefore very probable, *a priori,* that the crystallization of plaster is produced by the same means, or if this is not the case, it is absolutely necessary that an intermediate state exists during which the molecules of plaster possess a freedom of motion analagous to that which solution will impart to them. There is no example of solid bodies taking a crystalline

form without change of state.* The difficulty of admitting that the crystallization of plaster may be preceded by its solution arises from the fact that the quantity of uncombined water contained in mortar, which is about 20 per cent., is sufficient to dissolve only 1/2500 of the calcium sulphate with which it is mixed, and the reason is not seen why this salt when in solution should precipitate and thus allow the water to dissolve a new quantity.

It seems to me that this difficulty may be very easily overcome by relying upon the following experiment of M. Marignac. This savant has noticed that if a solution of calcium sulphate is prepared by agitating calcined plaster with a certain quantity of water and filtering the liquid at the end of about five minutes, a solution about five times as concentrated is obtained as if it had been prepared from calcium sulphate hydrated with two molecules of water. But this solution quickly becomes cloudy, deposits crystals of gypsum, and at the end of a longer or shorter time returns to its normal concentration. The saturated solution of dehydrated calcium sulphate is therefore supersaturated by comparison with the hydrated sulphate.†

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*The false crystalline forms obtained by M. Spring by compressing solid bodies are only the sliding surfaces produced by the rubbing of the body upon the walls of the mould. The experiments of M. Fizeau upon the compression of precipitated silver oxide, made much previously, however, to those of M. Spring, have been conclusive in this respect.

† The intervention of the phenomenon of supersaturation has been used by M. Landrin (Ann. de phys. et de Chim, 5e série, t. III, p. 441), in a very complex theory of the setting of plaster. This author assumed that plaster after being heated gave a saturated solution of calcium sulphate which became super-saturated afterwards in concentrating by evaporation; this evaporation would be the indispensable condition of hardening. In order to demonstrate the inaccuracy of this theory, it suffices to put plaster, tempered with water, in a hermetically sealed vessel where all evaporation is impossible, the

The physical phenomenon of the crystallization of plaster during its setting would then be as follows: calcined plaster is hydrated in contact with the water, which has been used to temper it, and gives a solution which soon allows the hydrated sulphate to crystallize, and then becomes able to dissolve new quantities of dehydrated sulphate. The phenomenon continues in this manner until the complete hydration and crystallization of the plaster. Indeed, these two contrary actions occur simultaneously at adjacent points. A continuous solution of new quantities of plaster compensates for the impoverishment of the liquor resulting from the equally continuous deposition of the hydrated crystals. The degree of concentration at which the solution is maintained depends upon the relative speed of these two contrary phenomena. When the hydration is very slow, the supersaturation is weak. When it is rapid, on the contrary, the supersaturation is considerable.

If this explanation is the true one, it must follow that the points where the hydrated crystals deposit are not necessarily in the place occupied by the grains of plaster. This is what has been confirmed by following the hydration under the microscope. Large needles are seen to form in the middle of the voids filled with water.

In order to demonstrate in an incontestable manner the reality of the momentary solution of all the calcium sulphate, it would be necessary to produce the crystallization entirely outside of the mass of plaster. I have not been successful in my experiments with this salt, but I have

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setting is seen to occur as rapidly as in the air. Moreover, the quantity of plaster which could thus crystallize by evaporation would be only a negligible fraction of the total mass.

with anhydrous sodium sulphate, a much more soluble salt which also sets similarly in contact with water.

M. de Coppet* has shown that when placed in water, it gives strongly supersaturated solutions even when care is taken to *prevent any rise of temperature.* This fact has been denied, *a priori,* by M. Gernez,† who attributes the supersaturation to a simple rise of temperature, but at different times I have verified the correctness of the M. de Coppet's assertion, both with the sodium sulphate and carbonate. Therefore a complete analogy can be established between the behavior of these salts and calcium sulphate, for which the elevation of temperature certainly plays no rôle, inasmuch as it does not notably change its solubility.

With sodium sulphate the crystallization of the hydrated salt at a distance is easily obtained by utilizing the greater density of the supersaturated solution. In a glass tube one centimeter in diameter, divided in mid-height by a metallic partition and full of water, I placed sodium sulphate melted and broken into pieces of the size of a pea. It is necessary that the fragments shall not be too small, in order to allow the facile circulation of the liquid, on the one hand, and to avoid the rise of temperature which would result from the simultaneous hydration of too large a quantity of salt, on the other hand. The tube is plunged into a considerable mass of water, and I have assured myself that under the conditions of my experiments the rise in temperature did not exceed half a degree. At the end of some hours there is formed at the base of the tube, that is, below the metallic partition, and several

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*C. R. LXIII., p. 1324.

†*Ann. de l'Ecole Normale*, 1878, 2e série t. VII., p. 67.

centimeters from the anhydrous salt, crystals of the hydrous salt which gradually fill the tube through its entire diameter. The set, the hardening, results precisely from the formation of this solid and coherent mass. In the normal conditions of setting this crystallization is produced at the outset in the interstices existing between the grains of the anhydrous salt, and afterward in those which are produced by the progressive solution of these same fragments.

I will speak here, incidentally, of cements and similar products, in order to avoid repeating the same thing when taking up the study of each of them.

Barium silicate, which hydrates upon contact with water, in setting gives supersaturated solutions, which, rapidly filtered and protected from the carbonic acid of the air, allow the crystallized hydrous silicate to deposit.

Again, it is the same with the different calcium aluminates which contribute to the set of the cement.

These experiments clearly show that in the case of salts, which set by simple hydration, that the crystallization is the result of the previous production of a supersaturated solution. We have the same thing when the set does not result from a simple hydration, but from the reaction between two different compounds in the presence of water.

M. Sorel has shown, in 1855, that a concentrated solution of zinc chloride added to zinc oxide gives at the end of a short time a solid mass of oxychloride having a considerable hardness. I have noticed that by using an excess of zinc chloride and filtering, after five minutes' agitation, the liquor which has not yet solidified, that crystallized oxychloride will be deposited after standing 24 hours, forming between the walls of the phial a coating a millimeter thick: the solution was therefore very supersaturated.

Likewise a solution of calcium chloride agitated with a solution of calcium hydrate and then filtered, allowed voluminous crystals of calcium oxychloride to deposit.

M. Ditte* has shown that pulverized gypsum, tempered with a saturated solution of potassium sulphate, congeals to a solid mass. I have noticed that the solution filtered after five minutes' agitation and before the beginning of the set, becomes filled, at the end of some hours, with crystals of double sulphate. In this case the supersaturation is so strong, and as a result the crystallization so abundant, that the filtered liquid becomes pasty in consequence of the large quantity of crystals which are held in suspension. The phenomena are exactly the same, for the double iodide of lead and potassium.

All of the compounds arising in the preceding experiments are strongly hydrated, but still the same phenomena of supersaturation are obtained in the formation of anhydrous compounds. Thus calcium carbonate is very easily obtained supersaturated by agitating calcium hydrate with a solution of an alkali carbonate and filtering the liquor at the end of a few moments. The conclusion to be drawn from all of these experiments is therefore that the crystallization which accompanies the set of all of the bodies hardening upon contact with water, results from the previous production of a supersaturated solution.

The formation of these supersaturated solutions is very simply related to the general laws of the phenomena of solution which I have established in a former work.†

I have shown that if we call

S the solubility-coefficient of the salt,

* *Ann. de l'École Normale*, 1876, 2e série, t. V., p. 102.

† *Comptes rendus*, t. C., p. 50.

Q the molecular heat of solution to saturation,
T the absolute temperature
we have the relation

$$\log S = M \int \frac{Q}{T^2} \, d\,T + K.$$

For another hydrate of the same salt we will have

$$\log S' = M \int \frac{Q'}{T^2} \, d\,T + K'.$$

whence may be drawn the relation of the two solubilities

$$\log \frac{S}{S'} = M \int \frac{Q-Q'}{T^2} \, d\,T + K-K'.$$

But experiment shows that conforming to a general law of the equivalence of systems in chemical equilibrium,* the solubility-coefficients of hydrates are the same at their temperature of reciprocal transformation.

By calling this temperature T_0 it becomes,

$$\log \frac{S}{S'} = M \int_{T_0}^{T} \frac{Q-Q'}{T^2} \, d\,T$$

For plaster, the temperature of transformation is about 130° C. whence

$$T_0 = 273 + 130 = 403$$

The heat of dehydration, $Q - Q'$, is about 1.8 cal.

These numbers substituted in the above equation show that at 15° the relative solubility of calcined plaster to that of gypsum is in the neighborhood of 7.

Mr. Marignac had found by experiment the ratio 5: these two numbers are as concordant as could be desired,

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**Comptes rendus*, Juin, 1886.

considering the slight stability of this solution which begins to desaturate with very great rapidity.

It is therefore well established that the crystallization which accompanies the hardening of mortars results from the difference in solubility of the bodies which set and those which are formed during the set; the former occurring in a state of unstable equilibrium in the presence of water and being able to exist there only momentarily.

The production of supersaturated solutions plays another rôle still in the phenomena of hardening by influencing the form of the crystals which are precipitated. These very frequently, under these conditions, become abnormally developed in one direction and then occur in the form of long, extremely slender prisms, true threads whose length may exceed one hundred times their thickness. It is thus that sodium acetate, sulphate and hyposulphite crystallize from their supersaturated solutions, salts which under normal conditions occur in crystals equally developed in all directions. The slender crystals do not remain isolated but group themselves around a central point, uniting by one of their extremities. The other extremities of the crystals form a practically spherical surface which remains so during the entire duration of the crystallization. The crystals which are produced during the set of mortars always occur in spherical groups like those which I have just described, but frequently the crystals are so slender that recourse must be had to the strongest powers of the microscope to distinguish them. For example, with plaster under the normal conditions of set, the crystallization is difficultly discernible and to show it, it is necessary to temper the plaster with water containing alcohol which retards the hydration and allows the crystals to attain a more considerable development. The calcium potassium

double sulphate, on the contrary, gives groups almost a centimeter in diameter in which each of the crystals can be seen by the naked eye.

Therefore, the crystals which are formed during the hardening are frequently, if not always, extremely small crystals, slender prisms joined by one of their extremities around central points in such a fashion as to form small spherical groups.

The solubility of bodies placed to harden in contact with water evidently influences the rapidity of the crystallization, and consequently, that of the set. Calcium sulphate which is relatively soluble sets more quickly than calcium aluminate, which likewise sets more rapidly than calcium silicate. I have noticed that by dissolving in the water used, substances which tend to increase the solubility of the substances mixed with the water, that the rapidity of the set of these latter is increased. Sulphuric acid and sodium hyposulphite produce a similar effect upon plaster:

	Setting time of plaster.
Pure water	15 minutes
Solution of $Na_2S_2O_3$ 1%	11 "
do 3%	8 "

HARDENING. I have in the preceding paragraph connected the *physical* phenomena of *crystallization* with the *chemical* phenomena of *hydration*. I propose now to show how the *mechanical* phenomena of *hardening* can be connected with the crystallization.

In studying this question, I have allowed myself to be guided by the preconceived idea that the hardening of mortars cannot be an isolated fact or without analogy, and that it is certainly like, and perhaps identical to, one of the known modes of hardening. All of these; *hardening*

by the compression of a pulverulent substance; by the *desiccation* of a pulverulent substance (clay) or of a colloidal substance (gelatine); by fusion and *solidification* (metals); and by *crystallization* (soluble salts); may be traced back to more simple and more general phenomena.

The mutual *adherence* of solid particles when brought into close contact and;

The mobility of these same particles which permits them to approach each other.

These are the two factors, the rôle of which in the hardening of mortars I believe ought to be studied. As to the mobility, the problem is solved by what I have said of the physical phenomena of crystallization. That is, the momentary solution of the salt which sets, gives the necessary mobility. The set of mortars evidently enters into the category of the phenomena of hardening by solution and crystallization.

After the solid particles have been brought into intimate contact the final hardness will depend upon the internal *cohesion* of the crystals and upon their mutual *adherence.*

The cohesion of different bodies varies within very wide limits, the two extremes of which among the bodies entering into the composition of various mortars are: *Plaster* for which it is rather weak, allowing it to be scratched by the finger nail, and *quartz,* which is hard enough to scratch steel.

The cohesion of bodies is an ultimate quality of matter, which we are not able in the present state of our knowledge to connect with any more simple and more general fact. Therefore, we cannot push our analysis of the hardening of mortars farther in this direction.

ADHERENCE, contrary to cohesion, is a very complex and

consequently very variable phenomena. Its variations are sufficient to explain the considerable differences in strength which similar mortars often show.

It varies with the *chemical nature* of the bodies in contact; a crystal of calcium sulphate has absolutely no adherence to a glass plate upon which it is formed. The adherence is *zero* but it is, on the contrary, so great with barium silicate that the crystals break rather than tear away from the glass. It varies also with the physical state, the more or less perfect polish of the surfaces in contact.

The total adherence is evidently proportional to the extent of the surfaces in contact; it will be the greater: *a* as the volume of the voids arising from the excess of water used in mixing the mortar is less, *b* as each crystal, for a given weight of material offers a greater development of surface. The form of elongated prisms which I have noticed in the crystallization of plaster and all similar products, is therefore, eminently favorable to the development of adherence; *c* as the crystals are grouped in such a way as to increase the volume of voids by diminishing their number and by isolating them from each other. A distribution of voids like that of pumice stone would be particularly favorable. But very slight variations in the external conditions; as the nature of the solvent, the temperature, and the crystalline particles present, modify considerably the conditions of development of the crystals and might consequently exercise a similar influence upon the final strength of the mortar.

PART II.

BARIUM CEMENT.

The analogies between lime and baryta allow the prediction of compounds of barium possessing properties analogous to those of the calcium cements, that is, susceptible of setting under water. I have noticed, indeed, that silica and baryta can combine to produce hydraulic compounds. These products have no industrial interest in consequence of the high price of baryta, but from a theoretical standpoint they are interesting to study, for the sake of the information which they can furnish upon the corresponding calcium compounds whose preparation is much more difficult.

I have begun with the study of the anhydrous and hydrous barium silicates, which have not been prepared hitherto.

Anhydrous silicates. All of the protoxides combine with silica in at least two proportions to give anhydrous salts of the formulas:

$$SiO_2.MO \text{ and } SiO_2.2MO.$$

The corresponding barium silicates can be prepared by melting in a common plumbago crucible a mixture of silica and anhydrous baryta in the desired proportions.

Mono-barium silicate, $SiO_2.BaO$, is easily fusible in a wind furnace, but however a little less easily than the corre-

sponding calcium silicate. It appears, after cooling, in the form of a compact mass with a crystalline fracture. When cut in thin sections and examined by the polarizing microscope, it shows a confused massing of long prismatic crystals without clear contours, with weak double refraction and with easy cleavage.

Di-barium silicate, $SiO_2.2BaO$, sinters in the wind furnace without complete fusion; when cold, it gives a porous mass which can be cut into a thin section only with difficulty, and in the polarizing microscope gives only the appearance of a confused crystallization.

Hydrous silicates. The simple hydrous definite silicates which are known are not very numerous and conform to one of the two formulas:

$$SiO_2.MO.Aq., \text{ and } SiO_2.2MO.Aq.$$

that is to say, to the formulas of the anhydrous silicates, plus water.

I have tried to obtain the corresponding barium silicates but have only been able to prepare those which contain one molecule of the base, the formula of which is

$$SiO_2.BaO.6H_2O.$$

I prepared it by precipitating baryta water by a solution of sodium silicate or of colloidal silica.

The precipitate at first is extremely voluminous and under the microscope does not show any crystalline appearance. It is therefore what is called an amorphous precipitate. It is, however, very probable that it is crystallized, but that the rapidity of the precipitation and its slight solubility make the crystals too small to be visible even under very great enlargement.

At the end of twenty-four hours, this precipitate of barium silicate changes its appearance completely; it collects at the bottom of the liquid in a very thin layer of tabular crystals visible to the naked eye. This crystallization of precipitates is, moreover, a very common occurrence. The physics of this phenomena is completely analogous to that which I have noted in the set of mortars. At the moment of the precipitation of barium silicate it is not the most stable variety of this salt, and as a consequence, the least soluble one, which is formed, but rather, either a particular hydrate, as is often obtained with strongly supersaturated solutions of sodium sulphate, or a dimorphic variety, as is obtained with supersaturated solutions of potassium nitrate and sodium chlorate in water, and of mercuric iodide in alcohol. After the precipitation of this more soluble variety, the solution remains supersaturated in comparison to the more stable variety and as a consequence may allow the latter to crystallize in turn; the concentration is thus diminished, a certain quantity of the salt first precipitated redissolves and the solution becomes supersaturated with respect to the second salt, of which it may allow a new quantity to crystallize and continue thus until the complete transformation of the precipitate. In reality, these two phenomena of solution and crystallization occur simultaneously, but at different points. The new crystals formed will be larger as the transformation has been slower. It is exactly the same process as that of the crystallization of plaster and all mortars.

The accuracy of the interpretation which I have proposed for this phenomenon can be verified by following under the microscope the transformation of salts which are sufficiently soluble to allow the first precipitate shown to

appear already clearly crystallized. The crystals of the first precipitate are seen to dissolve and be eaten away completely, in proportion to the formation of the second variety. The experiment is very clear with the double oxalate of copper and potassium and especially with mercuric iodide precipitated from its alcoholic solution.

By cooling the hot saturated solution of the red iodide, a crystalline precipitate of the yellow iodide appears, presenting itself everywhere in large thin laminæ.

These, if allowed to remain in a little of the alcoholic liquid in which they were formed, corrode gradually at the end of some hours, and in the middle of the cavities small crystals of the red iodide develop, which grow in proportion as the yellow laminæ corrode, until they completely disappear.

The precipitate of barium silicate finally obtained has a composition which can be represented by the formula

$$SiO_2.BaO.6H_2O.$$

as the following analysis demonstrates:

	Observed.	Calculated.
SiO_2	18.2	17.7
BaO	45.5	45.2
H_2O	35.3	37.1
	99.0	100.0

In different analyses, the proportion of water has varied from 6 to 7 molecules. I have taken the lesser number, because it is rather liable to errors of excess resulting from the presence of water occluded by the crystals.

The crystals may be obtained relatively voluminous and adapted to crystallographic determinations, by causing to react by diffusion, superposed solutions of sodium silicate

and barium hydrate. M. Mallard has kindly consented to determine these crystals.

Orthorhombic crystals:

$$a : b : c = 1.1723 : 1 : 0.6628.$$

Acute positive bisectrix normal to h_1.

Plane of the axes perpendicular to g_1. Dispersion $\rho < v$. Double refraction weak.

Angle of the axes in the air for yellow light 59° 40′.

I have observed that the formation of the salt disengages

$$\text{Gelatinous } SiO_2 + \text{dissolved } BaO = 4 \text{ cal.}$$

This salt is decomposed by water, as all the salts of weak acids generally are. The decomposition stops at 15° C, when the quantity of baryta contained in a liter of liquid is 0.91 grams.

Prolonged washings made with a sufficient quantity of water lead to the complete decomposition of this salt and leave a residue of pure silica. In washing with water a portion of the silica goes into the solution along with the baryta.

The neutral barium silicate is slightly soluble in water containing a sufficient quantity of baryta to prevent its decomposition. The presence of silica in the liquid is shown by means of lime water which immediately gives a white milky precipitate resulting from the much greater insolubility of calcium silicate.

This same barium silicate is produced spontaneously in laboratory flasks of baryta water at the expense of the silica of the glass. It then occurs in rather voluminous crystals adhering strongly to the sides of the flasks. The

nature of these crystals in flasks of baryta water had been recognized before my researches, but without my knowing it, by M. Pisani.* This savant had analysed and had given their crystallographic characteristics, but as a result of an error of the decimal point in his calculation, he attributed to them the incorrect formula:

$$3\ BaO.2SiO_3 + 2H_2O. \text{or}\ BaO.2SiO_3 + 2Ba(OH)_2.$$

I have tried without success to obtain the silicate with two molecules of the base

$$SiO_2.2BaO.Aq.$$

This result is not at all surprising; it is in accord with what we know of the decreasing stability of the salts of the same polybasic acid.

The calorimetric experiments of M. Berthelot have shown that boric, phosphoric acids, etc., give with the alkalies, basic salts very easily decomposed by water; only a small quantity of these are formed by virtue of the solubility of all the decomposition products which allow these latter to remain present and in consequence to limit the decomposition. In the case of the salts of barium, mono-barium silicate, which evidently is one of the decomposition products of di-barium silicate, being insoluble, separates out of the field of reaction, conformably to Berthelot's law, and allows the decomposition to be continued indefinitely. This experiment does not prove, therefore, the non-existence of hydrates of di-barium silicate, but simply the impossibility of obtaining them in the presence of liquid water, that is to say, from the special

* *Comptes rendus*, 27 novembre, 1876.

standpoint with which I am concerned in the conditions peculiar to the set of cements.

Barium cements. The most simple of the barium cements is that which is obtained by pulverizing anhydrous mono-barium silicate, $SiO_2.BaO$, obtained by fusion and tempering it with water. The set results from a simple hydration

$$SiO_2.BaO + 6H_2O = SiO_2.BaO.6H_2O.$$

The reaction which causes the set is therefore identical with that which occurs with plaster, and likewise for the processes of the crystallization and of hardening. Di-barium silicate, $SiO_2.2BaO$, also sets in contact with water. It gives a compact, somewhat translucent mass traversed in every direction by large lamellar crystals, the sections of which are very clearly seen upon the fractured surface of pieces of the cement. By allowing the set to take place under a layer of distilled water in a hermetically sealed vessel, the surface of the cement bristles with crystalline laminæ which are likewise the prolongation of those crystals which traverse the mass. By detaching them carefully by means of pincers and analysing, I have found crystals of barium hydrate contaminated by a little silicate

BaO	43.7
H_2O	52.0
SiO_2	3.0
	98.7

By comparing this formation of free baryta with the impossibility of obtaining di-barium silicate in the presence of water, it is concluded that the reaction which brings about the set is a splitting up of the anhydrous silicate according to the reaction

$$SiO_2.2BaO+15H_2O=SiO_2.BaO.6H_2O+BaO.9H_2O.$$

This reaction has a particular interest from the standpoint of the study of the calcareous cements; the set of these, as I will demonstrate farther on, results also from the splitting up of a basic calcium silicate in the presence of water, with the formation of large crystallized laminæ of calcium hydrate.

Calcined silica and pulverized barium hydrate tempered with the smallest possible quantity of water, still set as a result of the combination of these two bodies

$$SiO_2 + 9BaO.H_2O = SiO_2.BaO.6H_2O + 3H_2O.$$

The difficulty noticed with plaster from the incomplete combination of the water is here even more exaggerated. The equation of the reaction shows that not only does no part of the water used enter into the combination, but even a part of that combined with the baryta is released. The breaks of continuity occasioned by the presence of this liquid water are therefore more considerable than for any other mortar.

To sum up: the set of all the silicious barium cements results from the formation of one hydrous barium silicate.

$$SiO_2.BaO.6H_2O.$$

which may be produced by various reactions.

Either by the hydration, per se, of anhydrous monobarium silicate:

Or by the splitting up of more basic anhydrous silicates with the liberation of baryta.

Or by the direct combination of silica and baryta.

PART III.

CALCAREOUS MORTARS.

The calcareous mortars are divisible into two categories:

Air mortars; and

Hydraulic mortars.

I shall say only a few words of the first.

I have studied these only so far as they might throw some light upon the hydraulic mortars, the only purpose that I have in view here.

AIR MORTARS

These mortars are made with sand and slaked lime, that is, pulverulent calcium hydrate obtained by the action of water upon quick lime. Their set, as Vicat has shown, results entirely, at least in their first stage, from dessication which brings into intimate contact the extremely tenuous particles of lime. This phenomenon is identical with that of the hardening of clay. The sand acts in the same way as when it is added to clay for brick making. It prevents the shrinkage, which would necessarily accompany the desiccation, from being felt throughout the entire mass, and which would be shown by cracks in the mortar throughout its thickness, preventing any solidity. The grains of sand in contact form an incompressible matrix which prevents the shrinking from taking place except in the intervals existing between these grains and producing thus dis-

continuous voids which diminish, it is true, the full section and in consequence the strength, but no where causes a complete break in continuity.

It is seen why these are called air mortars; evidently they cannot ever harden under water, nor in any other places where evaporation will be impossible. Similar mortars five hundred years old have been found in the middle of massive blocks of masonry as soft as the day they were used. If these mortars, after drying out become wet, they soften again and lose all consistency. Therefore, up to this point they will show no advantage over mortars made with clay. But a second stage of hardening exists for fat lime mortars called the *period of carbonation* during which they considerably augment their strength and lose their alterability under the influence of rain water. This modification results from the absorption of carbonic acid from the air which transforms the calcium hydrate into carbonate; it occurs very slowly and always remains superficial; it only occurs under favorable conditions; the mortar must be moist but not, however, soaked with water.

Calcining the lime.—Lime is obtained by the decomposition of calcium carbonate under the influence of heat. It has been known since the experiments of M. Debray that this decomposition is in accord with the laws of dissociation, that is to say, that it limited to a temperature given by the definite vapor tension for carbonic acid. But precise numerical determinations on this subject are still wanting. I have purposed filling up this gap. For measuring the temperature I have used a platium-rhodium thermo-electric couple, connected with an aperiodic galvanometer of MM. M. Deprez and d'Arsonval.*

*Le Chatelier, De la mesure des temperatures élevées par les couples thermo-électriques. (*Bull. de la Soc. de phys.; juliet, 1886*).

It was probable by analogy with what I have observed in the calcination of gypsum, that the temperature of rapid calcination of limestone would be above that of its dissociation at atmospheric pressure. I have first determined this temperature of calcination by placing the joint of the couple in the middle of a small mass of pulverized calcium carbonate and studying the law of absorption of heat as I have done for gypsum. I have observed a point of halting sufficiently marked varying from 890° C. to 930° C. for the different varieties of calcium carbonate (precipitated carbonate, chalk and marble). The industrial calcination of the lime, taking place more slowly, ought to require a temperature of 890° at most; this number is an upper limit, just as the figure 128° C. which I have obtained for the calcining of plaster. When the calcium carbonate carries magnesia, a heating point is observed near to 720° C. which corresponds to the decomposition of magnesium carbonate.

Before taking up the complete study of the dissociation of calcium carbonate, I have made some preliminary researches upon the rapidity with which the equilibrium is reached. We have known that one of the chief causes of error in researches of this nature, comes from the fact that generally sufficient time is not waited to allow it to come to equilibrium. The preliminary experiments have shown me that at the same temperature the limiting tension is the same for precipitated carbonate, chalk and marble, but that the limit is much more rapidly reached with the precipitated carbonate; therefore, I have used this exclusively for the final determinations. I have noticed, among other things, that at temperatures below 500° C. precise experiments become impracticable. At 500° C. the limit was reached only at the end of two hours, which

represents, having given the weight of the material and the volume of the apparatus, an hourly decomposition of only $\frac{1}{10,000}$ of the material experimented upon.

The definite experiments were made in a porcelain tube stuffed with precipitated carbonate in the heated part, and filled beyond with pieces of marble to diminish the free space. The couple was placed in the midst of the carbonate. The tube was heated in a furnace at a temperature so constant that in one experiment, lasting twelve hours, the temperature rose only 10 degrees from the beginning to the end of the experiment. The couple had been graduated immediately before the experiment by means of the boiling points of sulphur and selenium, and the melting point of gold.* That the couple had not met with changes during the course of the experiment was ascertained by determining with it the melting point of gold immediately afterward. The couple had been wrapped in a small piece of gold leaf, being placed in the carbonate, and as soon as the dissociation was complete, the temperature was gradually raised, obtaining the fusion of the gold foil in the same apparatus in which the experiments had just been made.

* The very precise determinations of boiling and melting points made in the last few years have led to a modification of the temperatures that I have used as fixed points for the graduation of my couples in my experiments upon the dissociation of calcium carbonate.

The melting point of gold corresponds to the temperature of 1062° C. and not 1045° C., likewise the boiling point of selenium is 650° C. instead of 665° C., and, lastly, the boiling point of sulphur is 445° C. instead of 448° C. The corrections my first determinations must undergo in view of these facts are, in short, scarcely important and hardly exceed the order of magnitude of the experimental errors.

GRADUATION OF THE COUPLE

	Temperature of the joint. Hot t degrees.	Temperature of the joint. Cold t_0 degrees.	Deviations of the galvanometer. N millimeters.
Boiling point of sulphur.........	448	28	32.0
Boiling point of selenium........	665	28	56.0
Melting point of gold before......	1045	28	98.0
Melting point of gold after.......	1045	28	98.5

These figures show that in the range of temperature considered, the curve representing the deviations as functions of the temperature may be replaced by its tangent, the equation of which is

$$N = -14 + 0.11\ (t - t_0),$$

an empirical formula which has served for the subsequent calculations.

The following table gives the positive final results:

DISSOCIATION OF C_aCO_3.

Galvanometer N millimeters.	Normal temperature t_0 degrees.	Temperature t degrees.	Pressure h millimeters
43.5	22.0	547	27
50.2	22.0	610	46
51.5	24.0	625	56
64.6	25.5	740	255
64.8	26.0	745	289
72.0	26.5	810	678
72.2	25.0	812	763
78.0	27.0	865	1333

These temperatures and pressures should, as we know, be represented by the known equation:

$$\log p + \frac{1}{AR} \cdot \frac{L}{T} = \text{constant}.$$

In admitting that the latent heat of reaction at constant

pressure L remains unchanged in the range of temperature considered, and by representing this equation by a curve whose ordinates are the logarithms of the pressures and the abscessæ the reciprocals of the temperatures, we ought to have a straight line. All the data, in fact, plot quite accurately upon a straight line except the first for which the pressure needs to be reduced 10 millimeters. It is extremely likely that there is an experimental error due to the entrance of small quantities of gas into the porcelain tube. This experiment had lasted three hours and it is difficult to find tubes which hold a vacuum several hours when they are heated to redness.

The equation cited above allows the calculation of the molecular heat of combination 2 ($CO_2 + CaO$)* in the experimental conditions of temperatures. Thus we find:

$$L_{750^\circ} = 28 \text{ calories.}$$

Whereas, at the ordinary temperature,

$$L_{15^\circ} = 38 \text{ calories.}$$

The discrepancy is in the direction which we might expect from the play of the specific heat.

The value of the heat of dissociation thus found, 28 calories, for one molecular weight of carbonic acid is in accord with a law which I have recently formulated† and which requires that the quotient $\frac{L}{T}$ should be sensibly constant and contained within the limits 0.021 to 0.026.

We find, indeed,

$$\frac{28}{273 \text{x} 812} = 0.025.$$

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* $C_2O_4 + 2CaO$.

† *Bull. de la Soc. Chim.*, mai 1887.

These figures show that the dissociation-tension is equal to the atmospheric pressure at about 812° C. The figure is notably lower than the temperature of rapid calcination which I have found equal to 890°. The industrial calcination, which is rather slow, must take place at a temperature intermediate between these two figures. In round numbers we may take 850° C.

HYDRAULIC MORTARS.

The hydraulic products are divided into three very distinct categories:

Cements.
Hydraulic limes.
Puzzolanas and fat lime mortars.

Cements.—Cements are obtained bv calcining natural or artificial mixtures of limestone and clay containing at least 21 per cent. and at most 27 per cent. of clay. Small pieces placed in water do not slake like lime, but if they have been finely pulverized previously, they set and harden by combining with a part of the water which has been used to mix them to a mortar and at the end of a sufficiently long time acquire a considerable hardness. Cements are divisible into the classes *slow-setting* (Portland) and *quick-setting* (Roman).

The former are burned at a much higher temperature than the latter and sufficient to soften them to such a degree that on their coming from the kiln they appear as compact scoriaceous particles, very difficult to pulverize. Their cost of production is very high, but likewise they attain the greatest strength of all the hydraulic mortars. Their slow setting, which lasts several hours, greatly facilitates their use.

Hydraulic limes.—The hydraulic limes are obtained by the calcination of natural or artificial mixtures of limestone and clay containing less clay than cement mixtures. They are characterized by their property of slaking like lime which dispenses with their mechanical pulverization before use. They set much more slowly and attain less hardness than cements. They have been used from the oldest antiquity, confounded with the fat limes, and it was only in 1818 that Vicat discovered the nature and properties of these limes.

Puzzolana mortars.—The puzzolanas are bodies which mixed with fat slacked lime, give to it the property of setting under water. These are essentially silicious compounds in which the silica is in part soluble in potash. The puzzolana mortars were invented by the Romans, who made great use of them, and since the Roman times they have remained up to the beginning of this (nineteenth) century, until the memorable work of Vicat upon the hydraulic limes, the only mortars regularly employed for works in water.

Historical.—Theoretical researches upon the constitution of hydraulic mortars have been numerous. I shall sum them up rapidly, discussing them in proportion to the value of the ideas which I shall obtain from them.

Smeaton,* an English engineer, reported in 1756 the presence of clay in the hydraulic-lime limestones, but this observation passed unnoticed. A distinguished practitioner, the designer of important works, he enjoyed a great reputation as an engineer, but had no authority as a chemist.

Several years later, the Swedish savant, Bergmann, hav-

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ing analyzed the hydraulic-lime limestones of Lena, found in them several percent. of manganese and attributed the hydraulic properties of the lime to the presence of this body. This opinion, because of the authority of the illustrious reputation of its author, was accepted without discussion.

Guyton de Morveau,* trying to verify Bergmann's ideas, analyzed the principal hydraulic limes of France; he found that all contained clay, but only one, manganese. He said, nevertheless, upon the authority of the Swedish chemist, that manganese was the cause of the hydraulicity of limes.

Saussure† did the same work for the limes of Switzerland and found none which were manganiferous.

He declared, nevertheless, upon the authority of Bergmann and Guyton de Moreau that manganese was preeminently the hydraulizing substance, but he timidly added that clay could in a certain degree replace the manganese completely, although being very inferior to it. He explained the action of the clay by assuming that it played the part of puzzolana, that is to say, that after the calcination of the limestones, there remained a mixture of quicklime and calcined uncombined clay; an erroneous opinion which, however, has been revived in recent years and given as new.

The first precise and exact observation upon the hydraulic limes is due to Collet-Descotils, Mining Engineer, Professor of Chemistry at the Ecole des Mines. In 1813 he gave in a note a few lines long inserted in the *Annales des Mines,*‡ the analysis of the limestones and the lime of

* Académie de Dijon, 1785.
† *Voyage dans les Alpes,* t. III., p. 192.
‡ *Ann. des Mines,* 1813, t. XXXIV., p. 308.

Senonches and called attention on this occasion to the fact that the silica of the lime was soluble in acids, whereas that of the limestone was not, which demonstrates that during the calcination there had been a combination of the silica with the lime. He attributed the hydraulic properties of the lime to the compounds thus produced.

It is some years later, in 1818, that Vicat* gave his first memoir upon the hydraulic limes. We know that to this engineer belongs by far the largest share in the development of our theoretical and experimental information on mortars. Seconded by the intelligent protection of M. Becquey, Director General of the Ponts et Chaussées et des Mines, he devoted himself exclusively to the study of this important question and succeeded in establishing the general constitution of limes and hydraulic cements, in defining the most favorable conditions for their manufacture and their use; so that he is justly considered as the creator of this industry which was not long expanding from France over all of Europe.

Going back to Smeaton's observation he demonstrated by numerous analyses that all the hydraulic limes are derived from argillaceous limestones and inversely that all limestones containing a suitable quantity of clay would serve for the manufacture of hydraulic limes. Lastly, he succeeded in obtaining the artificial hydraulic products by calcining previously prepared mixtures of lime and clay. Thus he demonstrated in an absolute manner that the hydraulic properties of lime were due exclusively to the presence of clay and demolished Bergmann's theory upon the rôle of oxide of manganese, a theory which was always in vogue, notwithstanding the numerous contradictions which it had received from experiment.

* *Recherches experimentales sur les mortiers en 1818.*

Generalizing Collet-Descotils' observation, he showed that the elements contained in clay formed with the lime certain compounds which alone possessed hydraulic properties. Lastly, he established by numerous analytic and synthetic experiments, that of the two elements of clay, the silica played the preponderating, if not the exclusive, part in the hardening of mortars.

All these conclusions have been fully confirmed by later researches, and little has been added to them. These results, however, incomplete as they were, still sum up almost all that we know upon the constitution of hydraulic mortars.

Immediately upon the publication of Vicat's researches, Berthier* repeated, with his habitual precision, the greater part of his predecessor's experiments, and confirmed their accuracy. He tried, furthermore, to determine the composition of the calcium silicate which is formed during the burning, by calcining in the laboratory mixtures of SiO_2 and CaO, and using the solubility of the free lime to separate it from the lime combined with the silica. This method, which has since been used repeatedly, cannot give an accurate result; it has caused three different formulas to be assigned to the calcium silicate:

Berthier	$SiO_3.CaO$
Rivot	$SiO_3.3CaO$
M. Landrin..........................	$SiO_3.2CaO$†

This method is faulty for the three following reasons:

1. It is impossible by a calcination of several hours to obtain in the laboratory the integral combination of the silica and lime—infusible bodies which give compounds equally infusible, if the lime is a little high in proportion.

*Ann. des Mines, 1822, 1re série, t. VIII., p. 483.

†One instantly notices in these formulas the direct influence of the formula SiO_3 formerly assigned to silica.

2. The anhydrous basic calcium silicates are partially decomposed by water with the liberation of free lime, this method, therefore, at the best, allows the determination of the formula of the hydrated silicate.

3. The hydrated calcium silicates themselves are completely decomposed by a sufficient excess of water, in such a way that they give upon analysis a variable composition according to the duration of the washing.

I will demonstrate further on each of these statements.

After Berthier, Rivot,* who succeeded him as Professor of Assaying in the Ecole des Mines, made extended researches upon the same subject, from which he thought he established as a fact that during the calcination of cements the two compounds

$$SiO_3.3CaO \text{ and } Al_2O_3.CaO.$$

are formed.

The setting would then result, as in the case of plaster, by the simple hydration of these bodies, forming the compounds

$$SiO_3.3CaO.6H_2O \text{ and } Al_2O_3.3CaO.6H_2O.$$

This theory is the one most in favor at the present day and the one generally taught; it is, however, in reality, only a simple hypothesis which owes its life to the name of its author much more than to the experimental proofs upon which it is based.

The method followed by this savant is that of Berthier, that is, the determination of the free lime by solution, only he has applied it to real cements, either calcined, or having taken set for a long time and not to laboratory products.

* *Ann. des Mines*, 5[e] série, t. IX., p. 505.

He thus avoided the inconvenience of working upon incompletely formed compounds, and which did not possess perhaps any of the properties of real cements. But, on the other hand, he found himself in the presence of even greater difficulties arising from the presence of a great number of different bodies, which always occur in the clays and limestones which are used industrially.

These experiments cannot be conclusive for the reasons which I have already given, the partial and progressive decomposition of calcium silicates by water. They are, moreover, defective in that Rivot assumed that iron oxide is simply an inert body, whereas, it acts as an acid and is combined with an important quantity of the lime. Lastly, the results of the analyses of calcium silicates are not very concordant, which is not surprising when we know that the experiments were conducted principally upon concrete blocks immersed a long time in the port of Marseilles, and that it is necessary in order to determine the composition of the silicate to distinguish in the proximate analysis of mortars that which belongs to the more or less calcareous sand used as gangue, that which arises from the alterations due to the sea water, and lastly, that due to the free lime.

M. Fremy,* starting from Rivot's work, has sought to verify synthetically the accuracy of a theory which rested exclusively upon the use of the analytic method. He failed completely in the reproduction of calcium silicate which would set in contact with water, but succeeded, on the contrary, with calcium aluminate. Thus he was led to attribute a preponderating influence to alumina in the hardening of hydraulic mortars. This theory was very

* *Comptes rendus*, 1865, t. LX., p. 993.

actively contested; the fact that the best hydraulic limes of France, (those of Teil, Senonches and Paviers), did not contain enough alumina to speak of, at most 2 per cent., was opposed to it. In a second work upon the same subject, M. Fremy succeeded in obtaining some calcium silicates which did set, not in contact with water, but in the presence of an excess of lime, that is to say, behaving like true puzzolanas, and he concluded thence that the silica in cements should form similar silicates, which being in the presence of an excess of free lime, react mutually by the wet way.

M. Fremy has therefore demonstrated that the calcium aluminates will set; that certain calcium silicates act like puzzolanas; these are in themselves very interesting facts, of which it is impossible not to take account in a study of the hydraulic products and to which I shall have occasion to return. But he has not proved in any way by these experiments that similar reactions may be the only ones which occur in cements nor that they do ocur in them at all.

Lastly, I will recall to memory the recent researches of M. Landrin and of M. Merceron upon the same subject.

M. Landrin,* in the space of one year, had proposed three different theories of the hardening of mortars. One is only a reproduction of that of Saussure; clay acted simply like a puzzolana. In the second, the hardening is attributed to the hydration of a fictitious silicate of lime, the *puzzo-portland* $3SiO_2.4CaO$. The third theory on the contrary, invoked the action of carbonic acid upon the mono- and di-calcium silicates.

M. Merceron† has proposed an entirely original theory

**Comptes rendus*, t. XCVI., p. 156 and 1229; t. XCVIII., p. 1053.
†*Association Française*, Grenoble, 1885.

which attributes the hardening to the desiccation of the clay under the influence of the heat disengaged by the hydration of the lime.

It results from this historical summary that the only facts established in a certain manner are:

The production, during the calcination of cements and hydraulic limes, of compounds of lime with silica, and probably alumina, which possess the property of hardening in contact with water, without our knowing anything exact concerning the nature of these compounds or of the action of the water.

If I lay stress upon the paucity of the results obtained by these eminent savants it is for the purpose of showing the difficulty of this study, and to excuse myself for publishing a work which does not allow of the formulation of conclusions upon this subject as complete as I should have wished. I do not pretend to have completely solved the problem which I have begun. I hope simply to have made known a rather large number of new facts which may serve as useful material for establishing some day a complete theory of the hydraulic mortars.

In beginning my researches upon the cements, I have allowed myself to be guided by the preconceived idea that all of the phenomena which reside in these bodies are of a purely chemical character, that is to say, they result from the mutual reactions of definite compounds giving birth to other definite compounds. These compounds may be mixed in variable proportions and be very difficult to separate from each other, but their existence is none the less certain, and by completely understanding them we should be able to formulate the complete theory of the hardening of the hydraulic mortars without it being necessary to

cause any mysterious force such as capillary affinity or any other, to intervene.

In this view, the proceeding to follow is to begin by studying, from the chemical and mineralogical standpoints, the diverse compounds of lime with silica, alumina, etc., to determine their characteristics and finally to try to recognize the presence of one or the other in the cements and hydraulic limes.

THE SYNTHETIC STUDY OF THE CALCIUM SALTS.

Lime.

CaO.—Anhydrous lime is obtained by the calcination of calcium carbonate, between 800° C. and 900° C., or of calcium nitrate at a dull red heat. Its essential property is that of combining directly with water with the liberation of a large quantity of heat and slaking, that is to say, swelling up, cracking and finally being reduced to an impalpable powder. This property plays a great rôle in the hydraulic mortars of which it causes the pulverization without any expense of mechanical force. On the other hand, it frequently causes the destruction of masonry in which products containing unslaked free lime have been used. It is therefore very important to recall here the conditions which make this slaking more or less energetic.

Water in the state of vapor, or, more exactly, moist air, gives a much more considerable increase in bulk than liquid water, but the rapidity of the slaking is less with water in the vaporous state as a result of the necessity for a progressive renewal of the vapor absorbed.

Certain products which set without swelling in contact

with liquid water, slake under the action of moist air; others, on the contrary, remain unaltered under the same conditions.

The rise of temperature increases enormously the rapidity of the slaking and the magnitude of the increase in bulk. Some products which contain only a little free lime and which give at a low temperature only a little swelling fissure in every direction when they are put in water. The compactness of the lime which modifies the extent of the surfaces in contact with the water exercises a very great influence upon the rapidity of the slaking. Lime calcined rapidly below 1000° C. slakes instantly when it is plunged into water. Heated white hot, it will take several minutes in slaking. Lastly, lime from the strongly calcined nitrate takes hours and even days to slake.

The homogeneous mixture* of foreign materials in the lime diminishes this property considerably. It has been noticed for a long time that the impure limestones give limes difficult to slake which are called *lean* limes. Similar products are very easily obtainable in the laboratory by fusing together quick lime with a small quantity of calcium chloride, or with calcium aluminate. For mixtures in suitable proportions, the products set with cold water and slake in hot water and moist air. Often the set in cold water is followed, in the long run, by air slaking which brings about the disintegration of the solidified mass. These are Vicat's "limited limes." The magnesian limes can be taken as very instructive examples of this kind of phenomenon. The Dolomites, double carbonates of lime and magnesia, give by normal calcination lean limes which are slaked with difficulty, but which, how-

* I mean by *homogeneous* mixture, that which occurs in solutions, the isomorphous mixtures and the glasses.

ever, are never susceptible of setting. By calcining them at a temperature above the melting point of iron, as is done in the making of linings for basic bessemer converter retorts, a crystalline compact rock formed by the juxtaposition of crystals of a compound or an isomorphous mixture of lime and magnesia is obtained. When finely pulverized and tempered with cold water, the product sets like a cement; on the contrary, when put into air and water vapor at 300° C. it slakes rapidly. Left in the air at the ordinary temperature, its slaking does not begin to manifest itself until the end of a year and afterward continues for years without reaching an end. Thus I have had in my laboratory for six years a fragment as large as my fist of this overburned magnesian lime, which is only slaked off a centimeter in thickness. The slowness with which this slaking occurs is important to recall in taking up the study of the slow destruction of cements in the air.

$Ca(OH)_2$—Calcium hydrate is one of the most stable hydrates that we know; when it is rapidly heated its stationary temperature of decomposition is found to be between 530° C. and 540° C. Its dissociation-tension, from experiments that I have made, does not reach an atmosphere until nearly 450° C. At 360° C. it still is only 100 millimeters of mercury. Below 100° C. it is an infinitely small quantity which completely escapes all our methods of observation. Thus calcium hydrate can be preserved indefinitely in dry air at the ordinary temperature and even upwards of 100° C. without efflorescing. It is only very slowly attacked at the ordinary temperature by carbonic acid, but its solution, on the contrary, absorbs the gas very rapidly.

We know that the solubility of this body in water is 1.3

grams per liter; it is, as we know, the most soluble of all the calcium compounds which can be formed in cements.

Simple Calcium Silicates—Anhydrous Silicates.

$SiO_2.CaO$.—This silicate has been known for a long time. It exists in nature, where it has been called wollastonite; it has been produced by different means in the laboratory. I have prepared it by fusing a mixture of lime and silica in suitable proportions in a common plumbago crucible. A very hard mass with crystalline fracture and full of cavities is obtained. When examined in a thin plate in the polarizing microscope it is discovered that the crystals are present in thin, wide plates, which, viewed through their edge, show a very strong double refraction, and, on the contrary, viewed through their depth a very weak double refraction, if any.

This silicate when finely pulverized and digested in the cold for several days, in pure water, in solutions of ammoniacal salts, or in lime water, does not undergo any kind of alteration, which demonstrates that it cannot take any part in the normal hardening of cements. It is rapidly attacked by the strong acids with the production of gelatinous silica; it is slowly attacked by the weak acids such as carbonic acid. Tempered with water charged with carbonic acid and left in an atmosphere of carbonic acid, it sets completely. This fact has also been observed by M. Landrin and has been the basis for one of his theories upon the set of cements.

$SiO_2.2CaO$.—The compound corresponding to this formula ought to belong to the family of Peridotes; it does not exist in nature, and has not been obtained until now in the laboratory.

I have produced it by the direct fusion of silica and

lime in suitable proportions. The temperature necessary to obtain the fusion is near the melting point of wrought iron. A mass is thus obtained, which withdrawn quite hot from the crucible is compact, very hard and can only be broken with difficulty by the hammer.

On the contrary, on letting the crucible cool before opening it, only a white pulverulent mass is found; identical in appearance with the mixture experimented upon. The combination is none the less complete because the action of acids gives immediately a deposit of gelatinous silica. The fact is that during the cooling a very interesting phenomenon occurred which can be observed by leaving in the air the mass which was taken out of the crucible while quite hot. The mass, absolutely compact at first, is seen to crack gradually, to swell up, to disintegrate progressively and finally to be reduced to a white powder like slaked lime in appearance. When examined under the microscope, this powder is formed of prismatic fragments with weak double refraction diminishing in the direction of their greatest length, and some times showing fine striae following this direction.

This phenomenon of spontaneous pulverization has long been known in the metallurgy of iron; it is observed with all blast furnace slags which are sufficiently calcareous. Hitherto, this pulverization has been attributed to the action of the atmospheric moisture which leads to a slaking of slags by hydration as it does with quick-lime. The same phenomenon is also observed in the manufacture of Portland cement. Frequently fragments of cement clinker withdrawn while hot from fire are seen to pulverize at the end of a certain time. This transformation would be accompanied by a disengagement of heat manifested in the dark by a new incandescence of the already cooled mate-

rial. The value of this powder as cement is very slight, therefore, its production is an important cause of loss in manufacture. The study of this question thus has a direct interest at this point.

I began by assuring myself that this property belonged to the silicate $SiO_2.2CaO$, and only to it, and consequently the spontaneous pulverization in cements and slags is a certain indication of the presence of this compound. By varying the relative proportions of silica and lime submitted to fusion, it is proven that the pulverization is the more slow and incomplete the more the composition corresponding to the formula above is departed from. The mixture $SiO_2.1\frac{1}{2}CaO$ gives some unpulverized fragments large enough to enable thin sections to be cut from them. The very brilliant edges with very strong double refraction indicate the presence of wollastonite. This shows in passing that the puzzo-portland of M. Landrin does not exist as a definite product and that it is only a mixture of the two silicates $SiO_2.CaO$ and $SiO_2.2CaO$, both of which keep their individual properties. By replacing part of the lime in the compound $SiO_2.2CaO$ by magnesia its pulverization is again diminished. For equal molecular ratios of lime and magnesia a mass is obtained which remains absolutely compact, hard and clearly crystallized, it is monticellite $CaMgSiO_4$. The addition of alumina and iron oxide also diminishes the pulverization. Thus it is that blast furnace slags often require many days to disintegrate and only occasionally give a coarse sand, very different from the impalpable meal produced by the pure calcium peridote.

What is the cause of the spontaneous pulverization of these di-calcium silicates; is there any means of connecting this phenomenon with some more simple and more general

fact? Hydration under the influence of atmospheric moisture must be eliminated at the very beginning, the calcium silicate in question is not altered by water. The air is also without action because the melted mass plunged while still hot into mercury disintegrates in the same manner. I have supposed for a moment that at a high temperature a compound unstable at normal temperature could be formed, whose decomposition would lead to its disintegration. According to this hypothesis, lime ought to be set free, and its presence could be recognized in the aqueous solution, but experiment has not justified this supposition.

A chance observation has put me in the way of the explanation which I had searched for in vain. Intending to prepare by fusion some crystallized potassium sulphate whose dimorphism M. Mallard was then studying, I noticed that this salt after its solidification retained as long as it was hot a great hardness comparable to that of the crystals produced by solution, but when completely cooled, it became so friable that a simple pressure of the finger sufficed to reduce it to powder. The small pulverized fragments observed by the microscope appeared in the form of finely striated plates which are separated from each other along a cleavage plane perpendicular to the axis. The phenomenon is therefore in every point comparable to that which the calcium silicate shows. In the case of potassium sulphate, there occurs at a nascent redness, according to the investigations of M. Mallard, an extremely clear reversible dimorphic transformation which is accompanied by numerous macles. These macles, or twin crystals, bring into contact different reticular planes, the proximity of which determines the internal molecular tensions which are augmented during the cooling as a result of the inequality of the coefficients of expansion. It is conceivable

that these tensions may bring about the disintegration of crystals having sufficiently easy cleavage. If really the dimorphic transformation of a solid body can be a cause of disintegration, more examples ought to be found among the very numerous cases of dimorphism known at the present day. It suffices to cite litharge, which ordinarily appears in the form of scales obtained by the slow cooling of molten lead oxide. This oxide is dimorphous; when hot, the stable variety is yellow, *massicot;* when cold, the stable variety is reddish yellow, *litharge.* The passage of the body from one of these states to the other during the cooling brings about its disintegration. But this phenomenon is most marked with the anhydrous double sulphate of copper and potassium. The pulverization takes place below 100° C., which makes it readily observable.

In regard to its chemical properties, the silicate $SiO_2.2CaO$ is distinguished from the preceding by the ease with which the ammoniacal salts decompose it in hot or cold, concentrated or dilute solution. The action of acids is, as it should be, still more rapid; the decomposition by carbonic acid and the set which results therefrom are much more rapid than with wollastonite, but water is always without effect either when cold or when hot. It cannot hydrate the silicate directly, or decompose it. In experiments prolonged over a month, the quantity of lime dissolved by water was so slight as only to give a slight cloudiness with ammonium oxalate. Lastly, I have ascertained that this compound tempered with water does not set. After six months a sample of paste enclosed in a tube to protect it from carbonic acid, crumbled immediately upon a simple pressure of the finger. However, I do not wish to say that at the end of a very long time, water may not exert some action, because it is known that

all the silicates, even the most acid ones, are slowly decomposed by water. These experiments nevertheless suffice to establish the fact that di-calcium silicate $SiO_2.2CaO$ can only take a secondary part, if any, in the hardening of cements.

$SiO_2.3CaO$.—Tri-basic silicates of protoxides are unknown, however some analyses of grappiers or hard burned lumps from silicious hydraulic limes have led me to foresee the existence of a silicate corresponding to the formula given above. But for a long time all my attempts to prove it synthetically have remained fruitless. The calcination of a mixture of silica and lime has given me only a mixture of calcium silicates and free lime. This latter is recognized by the rapid disengagement of heat and by the slaking produced by the action of water. But after slaking, the pulverulent mass, tempered with water, sets more or less slowly, thus behaving like a true hydraulic lime. This seems to indicate that among the silicates obtained there must be one which is different from the silicates previously studied. But this indication is too slight to base any conclusion upon.

I have hoped to obtain the best results by approximating the practical conditions of the manufacture of these cements, that is to say, by using a flux to facilitate the reaction of the silica and lime. Calcium chloride was clearly indicated by its great fusibility and its solubility in water and alcohol, which ought to allow its easy separation from the crystals. By using an excess of calcium chloride, I have obtained very pretty crystals, unchanged by alcohol, but very easily changed by water. These ought, therefore, to be crystals of cement.

Chemical analysis showed me that instead I was dealing with a calcium chlor-silicate:

$SiO_2.2CaO.CaCl_2$.

Chemical Analysis.

	Found.	Calculated.
SiO_2	20.5	21.2
CaO	59.6	59.3
Cl	25.4	25.4
	105.5	105.9
Subtract O = Cl	5.7	5.7

I have determined some physical properties of this compound:

Density	2.77
Melting point, near	800° C.
Molecular heat of solution in dilute HCl	36 cal.

M. Mallard has been kind enough to determine the crystals. They belong to the orthorhombic system and show the simple forms:

$$m=110;\ g_1=100;\ e_1=101.$$

A very clear cleavage parallel to h_1 exists, and one less clear, parallel to g_1

$$a : b : h = 1 : 0.726 : 0.287$$

Strong double refraction. Axis-plane g_1, negative bisectrix perpendicular to h_1.

Angle of the axes (in the air) about 25 degrees; $\rho > v$.

Calcium fluoride, used as a flux instead of the chloride, has proved no more satisfactory. The cold mass has always pulverized in cooling, a characteristic which indicates the presence of

$$SiO_2.2CaO.$$

A great number of attempts, pursued in the same manner, remained fruitless. I therefore find myself exactly

at the point where M. Fremy has stopped; the impossibility of obtaining in the laboratory a definite silicate of lime setting by the direct action of water.*

I then had the idea of starting from the calcium chlorsilicate previously obtained and decomposing it by water vapor at a temperature above 450° C., the normal dissociation-temperature of calcium hydrate. I obtained in this way the reaction

$$SiO_2.2CaO.CaCl_2+H_2O=SiO_2.3CaO+2HCl.$$

The decomposition is very slow and remains superficial. The mass must be pulverized repeatedly in order to obtain a nearly complete elimination of chloride. The purest product thus prepared had the composition

	Observed.	Calculated.
SiO_2 (by difference)	26.7	26.3
CaO (tested alkalimetrically)	72.1	73.7
$CaCl_2$ (tested by silver)	1.2	....
	100.0	100.0

This is a pulverulent mass, showing no evident trace of crystallization; it is not therefore possible to establish by fixed characteristics if we are really dealing with a definite compound, and consequently if it is identical to crystals of cement. But by finely pulverizing this mass, tempering it with water and allowing it to harden in boiling water, there is obtained at the end of eight days, briquettes which are comparable in hardness to those of cement, and showing no trace of swelling or cracking. This absence of swelling is a certain indication of the absence of free lime (because, in fact, if we added only 1 per cent. of strongly calcined free lime to a cement of good quality which does

* Mr. Newberry has succeeded in preparing this body directly by the fusion of its elements in the oxyhydrogen blowpipe, and he has obtained a material possessing all the qualities of a good Portland cement.

not swell in cold water, we observe a considerable cracking and a swelling of volume of about 10 per cent.). This characteristic, together with the property of setting which none of the lower silicates possess, shows clearly that we have to do with a compound and not a simple mixture whose properties would simply be the sum of those of the mixed bodies.

I pass by here the theoretical question whether it is a combination in definite proportions or a combination in variable proportions as the isomorphous mixtures are.

Silicious Glasses.—The fusion of mixtures of silica and lime containing less than one molecule of lime for one of silica produces glass, that is to say, homogeneous mixtures or mutual solutions of silica and calcium silicate. The crystals of wollastonite become more and more rare and unformed, in proportion as the silica is increased. They have almost completely disappeared for the mixture $SiO_2.\frac{1}{2}CaO$. These glasses are not attacked by water and are less and less attacked by acids in proportion as they become more silicious. The alkalies attack them slowly; with lime they can act like puzzolanas, but rather moderately, however; they thus behave like all silicious materials containing free silica. The presence of a small quantity of the alkalies increases considerably their action as puzzolanas. They ought to be the puzzolanic silicates obtained by M. Fremy.

Hydrated calcium silicate. $SiO_2.CaO.2\frac{1}{2}H_2O$.—Hydrated calcium silicate cannot be obtained in a pure state by the hydration of the anhydrous silicates, inasmuch as some of them are entirely unchanged in water and the others only very slowly attacked, but the method indicated by Guyton de Morveau at the beginning of this (nineteenth) century can be followed, precipitating an alkali

silicate by a lime salt, or by causing hydrated silica to react upon calcium hydrate. The precipitate thus obtained is amorphous and does not seem to have a definite composition. According to the relative proportions of lime and silica, we can obtain formulæ from $SiO_2.\frac{1}{10}CaO$ up to nearly $SiO_2.2CaO$. By working in the presence of an excess of lime, the composition of the precipitate which is less variable is still indefinite, inasmuch as the following different formulæ could be assigned to it.

$SiO_3.CaO$ or $3SiO_2.2CaO$.... ....Berthier
$SiO_3.2CaO$ or $3SiO_2.4CaO$.............M. Landrin
$SiO_3.3CaO$ or $SiO_2.2CaO$............ ....Rivot

In order to prepare this body in a pure state, I have precipitated a solution of colloidal silica by an excess of lime water; the precipitate formed is so voluminous that after complete deposition, one gram of this body still occupies a volume of two liters. The washings are thus made very tedious, but I have noticed further that the washings decompose it and take lime from it. By using a sufficient volume of water, we finally obtain a residue of nearly pure silica, but all the silica does not remain to the end of the operation, a part disappears in the washings, as had occurred with the barium silicate.

It was interesting to study this decomposition of the silicate by water as much for the purpose of determining its composition as for the purpose of considering the consequences which may lead to the destruction of cements by water. A certain weight of the hydrated silicate was suspended in almost saturated lime water; after settling, half of the liquor was removed, analyzed and replaced by pure water, and the same operation was repeated a certain num-

ber of times. The table herewith gives the experimental results:

Total quantities of lime removed. Grams.	Quantity of lime existing in solution in one liter of the liquor. Grams.
0.000	1.00
0.50	0.51
0.755	0.27
0.89	0.14
0.955	0.085
0.99	0.065
1.03	0.053
1.07	0.052

It is seen that the strength of the solution decreased at first proportionately to the volume of water added, or very nearly so; this indicates that the quantity of lime given to the wash water by the precipitate is sensibly zero. But when the lime content in the wash waters has fallen to 0.052 grams per liter, the phenomenon changes. The addition of new quantities of water no longer changes the lime content of the liquor, which remains fixed at 0.052 grams per liter. The silicate gives up its lime to the water up to a constant strength, thus conforming to general laws of the decomposition of salts by water.

In order to make an analysis of a definite calcium silicate it is therefore necessary not to carry the washing of it to the limit indicated above. Above this it would seem that we ought to find a precipitate of constant composition, but this is not the case. In the presence of saturated lime water and after a contact of six months, the composition of the precipitate approximates that indicated in the formula:

$$SiO_2.1.7CaO.Aq.$$

whereas at the first moment of its precipitation in a

liquid impoverished of lime by the very fact of its precipitation, it approximates the formula:

$$SiO_2.1.3CaO.Aq.$$

Lastly, by washing the precipitate and stopping at a lime content in the liquor a little higher than that for which the normal decomposition begins, the product

$$SiO_2.1.1CaO.Aq.$$

is obtained.

These facts lead me to assume that the normal composition of hydrated calcium silicate is, as for the barium silicate

$$SiO_2.CaO.Aq.^*$$

The lime in excess would be fixed by a phenomenon of superficial attraction well known for finely divided chemical precipitates, similar to retention of lime by the precipitates of alumina and oxide of iron, of potassium sulphate by barium sulphate, etc. The quantity of lime thus held necessarily increases with the concentration of the solution.

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*At the present day the formula

$$SiO_2 2CaO.Aq.$$

is quite generally assigned to the hydrated silicate formed during the set of cement.

But this is simply a matter of interpretation. The experimental determinations made upon the composition of these bodies are completely in accord with mine, that is to say, that always a little less than 2 molecular ratios of lime are found for 1 of silica. The number found being more nearly 2 than 1, this former number is chosen, but I persist in thinking that the arguments drawn from the progressive dissociation of the silicate by water are still valid and prove that an excess of lime is fixed in some other way than in the state of definite combination.

Analysis of the washed precipitate has given me as results:

Analysis.		Molecular Ratios.
SiO_2	36.4	1.21
CaO	35.7	1.28
H_2O	27.0	3.00
	99.1	

which leads, by deducting 1-15 of a molecule of $Ca(OH)_2$ to the formula

$$SiO_2.CaO.2\tfrac{1}{2}H_2O,$$

which I consider as the only hydrated and definite calcium silicate able to be formed in the presence of water and of an excess of lime. The formation of these salts disengages for one molecule of silica:

$$\text{Colloidal } SiO_2 + \text{dissolved } CaO = 6 \text{ cal.}$$

Calcium Aluminates.—The few definite aluminates which have been studied hitherto show very clearly that alumina is a poly-basic acid, several compounds are known of the form $Al_2O_3.MO$. The reaction of alumina upon sodium carbonate gives, as M. Mallard has shown, a compound of the same formula, $Al_2O_3.Na_2O$. In the presence of water, alumina and baryta give, according to H. Sainte-Claire Deville, the compound, $2Al_2O_3.3BaO.Aq$. Lastly, M. Fremy has shown that a solution of potassium aluminate deposits crystals having the formula

$$Al_2O_3.3K_2O.Aq.$$

It was therefore very probable *a priori* that several calcium aluminates ought to exist. Indeed, I have discovered at least three different ones.

$Al_2O_3.CaO$.—In order to study the anhydrous aluminates, I fused mixtures of alumina and lime in variable proportions; the melts obtained and cut into three sections have been examined in polarized light by the microscope.

Mono-calcium aluminate corresponds to a spinel and is difficultly fusible, has very great hardness and crystallizes in the cubic system. When reduced to a fine powder and tempered with water, it sets rapidly; suspended in a large excess of water, the alumina and the lime dissolve. I shall return more in detail to this action of water when discussing the following aluminate, which behaves in an analogous manner.

$2Al_2O_3.3CaO$.—Upon fusing a mixture containing 1½ to 2 molecules of lime for one of alumina, a rather easily fusible and very hard mass is obtained, which cut into thin sections shows crystals of very strong double refraction, belonging to the orthorhombic system (Fig. 5, facing page 86. There is therefore present a new definite aluminate different from the preceding. Unfortunately, however, the fused masses are not completely crystallized, even after recalcination, a vitrous part always remains which causes a little uncertainty to exist concerning the exact composition of the definite crystallized aluminate. The formula $Al_2O_3.2CaO$ can be adopted very well. I have allowed myself to be guided in the choice of the formula by that of the barium aluminate.

This calcium aluminate when finely pulverized and tempered with water sets with a rapidity comparable to that of plaster, but the hydrates thus formed have little stability because the mass heated to 100° C. in the presence of water disintegrates and sometimes ends by being reduced to mud.

When finely pulverized and agitated with a large excess of water, this aluminate allowed alumina and lime to dissolve in variable proportions. I will cite as an example the following analyses of the filtered solutions:

	Materials dissolved after 10 minutes' agitation.	
	Al_2O_3 grams.	CaO grams.
1 gram $2Al_2O_3.3CaO$ in liter of H_2O......	0.19	0.39
10 grams " " "	0.21	0.24

But this solution is supersaturated, it soon deposits crystals of the hydrated calcium aluminate and the larger part of the alumina is thus precipitated. Upon adding lime water to the liquor, the crystallization is immediate, and no more alumina remains in solution.

Upon introducing calcium aluminate in large crystals into the water, the action remains superficial; a crust of hydrated calcium aluminate about half a millimeter thick is formed which absolutely protects the internal core. After remaining in the water three years the depth of the hydrated layer does not seem to have exceeded that which it had reached at the end of two or three months. If instead of immersing the fragments of the aluminate, they are left in moist air, they are seen to crack gradually and then to be reduced to powder. They then undergo a true slaking, and this action continues for some years without reaching its limit.

$Al_2O_3.3CaO$.—Upon increasing the proportion of the lime in the mixture fused, the crystals with strong double refraction are soon seen to disappear. When the composition $Al_2O_3.3CaO$ is reached, the thin slabs cut from the fused mass cease to act upon polarized light. Nevertheless, some very clear outlines are seen showing that the

whole mass is uniformly crystallized. Therefore a definite aluminate exists corresponding to the formula $Al_2O_3.3CaO$ and crystallizing in the cubic system. It is the most fusible of the aluminates. When pulverized and tempered with water, it sets like the preceding aluminates.

This aluminate is equally soluble in water. Upon filtering after 10 minutes' agitation the liquid obtained by putting 1 gram of the aluminate in a liter of water I have obtained the following results:

	Al_2O_3 contained in 1 liter. grams.	CaO contained in 1 liter. grams.
Cold water at 15°	0.08	0.15
Cold water with 3% NaCl	0.12	0.40
Boiling water	0.03	Not determined.

For higher proportions of lime a molten mass is still obtained, inactive on polarized light, and slaking rapidly in moist air. When pulverized and tempered with water mixtures below $Al_2O_3.4CaO$ still set well; the more calcareous mixtures swell more and more, and finally are slaked like lime without taking any set. All of these characteristics indicate that we are dealing with a mixture of lime and aluminate of lime having the properties of these two bodies.

Hydrated Calcium Aluminates.—Several hydrated calcium aluminates exist. One of these which can be obtained by evaporating solutions of alumina and lime, very poor in lime, obtained by the action of water upon an anhydrous aluminate, has no interest from the standpoint of a study of cements, which after setting always contain an excess of free lime. I shall concern myself only with the most basic aluminate, the production of which in a state of purity is likewise the easiest.

$Al_2O_3.4CaO.12H_2O$.—The method of preparation which has given me the best results consists in starting with a filtered solution of anhydrous aluminate and in adding to it an equal volume of lime water. A white crystalline precipitate is immediately formed, which settles rapidly. In order to obtain solutions containing as much alumina as possible, it is well to start with a very slightly calcareous aluminate and to conduct the operations of solution and filtration as rapidly as possible. It is necessary to work with a dozen liters of liquid to obtain one gram of the precipitate.

When examined by the microscope, the precipitate appears in the form of long needles extending in the direction of their length and united around a central point in such a manner as to form spherical groups similar to those which are observed in the crystallization of all the supersaturated solutions. (Fig. 6, facing page 86). When the crystallization is so slow, compact spherolites are obtained, giving the black cross in parallel light similar to those which occur in the precipitation of calcium carbonate.

This calcium aluminate, washed with water, is decomposed by giving up lime and a small quantity of alumina; the decomposition is stopped at a temperature of 15° with a content of lime in the solution equal to 0.225 grams per liter. It therefore is a phenomenon similar in all points to the decomposition of the barium and calcium silicates by water.

The experiments have been carried out as with the silicate, by removing half of the supernatant solution and replacing it by pure water until the moment when the

alkatimetric strength of the liquid becomes constant. Here are the numbers obtained at a temperature of 17°:

Total weight of the lime removed from the liquor. grams.	Weight of lime contained in 1 liter. grams.
0.00	1.00
0.50	0.50
0.75	0.26
0.88	0.230
1.01	0.220
1.12	0.225
1.23	0.225

The analysis of different samples of the calcium aluminate, drained and pressed between filter paper has given me:

	I.	II.	III.	IV.	V.
Weight of material employed (grams)	0.1	1.0		0.5	0.664
Water	47.8 (diff)	39.2		40.8	38.4
Alumina	17.2	19.2	16.8	17.3	19.6
Lime	35.0	40.5	33.2	39.6	40.0
	100.0%	98.9%		97.7%	98.0%

These results lead to the following rough formulas:

I. $Al_2O_3.3.75\ CaO.15H_2O$.
II. $Al_2O_3.3.7\ CaO.12H_2O$.
III. $Al_2O_3.3.6\ CaO.14H_2O$.
IV. $Al_2O_3.4.2\ CaO.13.5H_2O$.
V. $Al_2O_3.3.7\ CaO.11H_2O$.

I have adopted the formula $Al_2O_3.4CaO.12H_2O$ as the most probable one, assuming *a priori* that the number of molecules of alumina and lime are in a simple ratio.

This is the only hydrated aluminate stable in the presence of an excess of lime; therefore, it is the only one which we can find in cements after their set.*

*Some later researches by M. Candlot have shown that the exact formula of this aluminate was $Al_2O_3.3CaO.Aq.$ and not $Al_2O_3.4CaO.Aq.$,

Calcaro-Magnesium Aluminates.—The substitution of a certain quantity of magnesia for lime in the mixtures submitted to the fusion gives crystallized products, the fusibility of which increases at first with the proportion of magnesia, passes a maximum and afterwards decreases, so that the pure magnesia aluminates are infusible. The alterability of aluminates by water decreases very rapidly by the substitution of magnesia for lime. Double salts seem to be formed, liberating a notable quantity of heat by their combination, and in consequence becoming much less sensible to the action of chemical reagents. This is an analogous fact to that observed with dolomite which is slightly attacked by acids, whereas the two carbonates which compose it taken separately are very easily attacked.

Calcium ferrites.—Iron sesquioxide combines with lime in the same manner as alumina and ought therefore to give

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as I had assumed. This body, therefore, is formed by direct hydration of tri-calcium aluminate and not with addition of lime.

It is almost certain that calcium ferrite has the same composition.

Calcium aluminate gives, with calcium chloride and calcium sulphate, two extremely important compounds, the existence of which has been noted for the first time by M. Candlot.

Calcium chlor-aluminate, the composition of which has been determined by Mr. G. Friedel, corresponds to the formula

$$Al_2O_3.3CaO.CaCl_2.10H_2O.$$

It is decomposed immediately upon contact with water, but seems to be capable of being formed momentarily by the action of saturated solutions of calcium chloride upon the anhydrous aluminates which explains the changeable solubility of these compounds.

Calcium sulpho-aluminate, the exact composition of which has been determined by Mr. Deval, corresponds to the formula

$$Al_2O_3.3CaO.3\ (CaO.SO_3).30H_2O.$$

It appears to be the principal, perhaps the exclusive, cause of the chemical decomposition of cements in sea water. But the method of its destructive action and of the swelling which it causes is yet unknown. (*Bulletin de la Sociétié d'encouragement*, juillet, 1890, and février, 1900.)

as varied products, but I have not succeeded in obtaining them.

When it is attempted to fuse a mixture of oxide of iron and lime in the proportion of a molecule of each, the very high temperature necessary to effect this fusion leads to the partial reduction of the sesquioxide to the state of the magnetic oxide of iron, even on making the flame as oxidizing as possible. On adding two or three molecules of lime, the mixture melts easily without reduction of the oxide. The melt is of such a dark color that cut into this section it is not sufficiently transparent to enable it to be studied by the microscope.

All of these calcium ferrites, when treated with water, swell and slake more or less rapidly and none of them take any set.

A hydrated calcium ferrite exists, to which Pelouze has assigned the formula $Fe_2O_3.4CaO.Aq$. It is a white substance which is very rapidly altered by carbonic acid, which colors it brown by liberating the hydrated sesquioxide of iron. It is decomposed by water until the lime content of the liquor is about 0.60 grams per liter. But the limit is much less clearly defined than with the calcium aluminate and silicate. I have been able to obtain this compound by the prolonged contact (about one month), of moist hydrated iron oxide $2Fe_2O_3.3H_2O$ and calcium hydrate, but I have never been able to prepare it pure enough to establish its formula and determine its water of hydration.

Calcium Alumino-ferrites.—The mixture of alumina and iron sesquioxide considerably augments the fusibility of the corresponding lime salts. Thus I have obtained the double salt

$$Al_2O_3.Fe_2O_3.3CaO$$

very clearly crystallized in long needles of a beautiful red color. It is truly a double salt and not an isomorphous mixture, because if more than one molecule of alumina is used, for one of the oxide of iron, colorless crystals of calcium aluminate are seen to be formed in addition to the red crystals.

I have tried, as for the calcium silicate, to cause the aluminates and ferrites to crystallize in a bath of molten calcium chloride; these attempts have been entirely fruitless. With the aluminates a vitreous very fusible material is obtained, which is alterable by water and dissolves calcium chloride, and leaves an insoluble gelatinous residue containing alumina. With the ferrites, on the contrary, very beautiful brown crystals are obtained, which are unchanged by water and dilute acetic acid and permit the easy separation of calcium chloride and of the excess of lime. But this compound is a chloro-ferrite:

$$Fe_2O_3.CaO.CaCl_2$$

Chemical Analysis.

	Observed.	Calculated.
Fe_2O_3	51	49.0
CaO	18	17.2
$CaCl_2$	32	33.8
	101	100.0

This body is very well crystallized, but it has such an easy cleavage that we can hardly gather anything but cleavage plates. I have found 129° 20′ and 109° 10′ for the angle of the cleavage plane with the two adjacent faces, which gives 121° 30′ for the prism angle. These plates are terminated by an obtuse systemmetrical pointing, the plane angle of which is 139°.

Multiple Silicates of Alumina, Iron and Lime.—The number of double silicates at present known is very considerable and still increases. I soon gave up pursuing in this direction the researches which I had begun. It is the least complete side of my work. But I will show later, that from the standpoint of the theory of cements these compounds only play a secondary rôle.

Among the double silicates the only interesting ones are those which contain the most lime; the acid silicates like the feldspars, which by fusion give glasses, cannot exist in cement. I have assured myself that mixtures of silica alumina and lime containing twice as much oxygen with the silica and alumina as with the lime, give upon fusion glasses which are unalterable in water. The mixtures containing an equal number of atoms of oxygen with the silica and alumina on the one hand, as with the lime on the other, give crystallized melts which, examined in thin sections, seem to be made up of two different kinds of crystals, the relative proportions of which vary with the proportions of alumina and silica. Some little cells with rounded contours and having weak double refraction, are essentially silicious, the others, elongated crystals, extinguishing in the direction of their length are essentially aluminous. I have not succeeded in determining the composition of either of them.

Lastly, I will recall that the most basic calcium double silicates which we know are formed in blast furnace slags. These are

Melilite.	$SiO_2.\frac{1}{6}Al_2O_3.1.3CaO$
Idocrase.	$SiO_2.\frac{1}{4}Al_2O_3.\ CaO$
Gehlenite.	$SiO_2.\frac{1}{2}Al_2O_3.1.5CaO$

all of which contain less than two molecules of lime to one of silica.

I have tried to obtain some hydrated double silicates; we know that the alkali silicates and aluminates combine with the liberation of some alkali, to form an insoluble silico-aluminate, the composition of which, according to H. Sainte-Claire Deville, may be represented by the formula

$$3SiO_2.Al_2O_3.Na_2O+Aq.$$

It was possible that the corresponding lime compounds might behave in the same manner. I have mixed precipitates of calcium aluminate and calcium silicate with lime water diluted with an equal volume of water, that is, of such a concentration that neither the aluminate nor the silicate can be decomposed by the sole action of the water. The mutual reaction of these two compounds ought to cause the strength of the lime solution to vary. I have observed nothing of the kind, which shows that either no reaction has occurred, or, if one did, the quantity of the combined lime did not vary, contrary to what happens for the alkali silico-aluminates.

To sum up, three different anhydrous calcium silicates exist, only one of which, the tri-calcium silicate, $SiO_2.3CaO$, is attacked by water and capable of taking set; three calcium aluminates, all of which take set very rapidly in water; some calcium ferrites, all of which slake and swell like quick lime, and lastly, numerous multiple silicates, none of which, amongst those so far studied, is alterable by water.

The only corresponding hydrated salts able to exist in the presence of an excess of lime are

the silicate $SiO_2.CaO.2\frac{1}{2}H_2O$.
the aluminate $Al_2O_3.4CaO.12H_2O$.
the ferrite $Fe_2O_3.4CaO.Aq$.

These salts are decomposed in the presence of an excess of water, liberating lime.

MICROCHEMICAL STUDY OF CEMENTS.

The cements and hydraulic limes contain variable proportions of their constituent elements: silica, alumina and lime; they therefore are not definite compounds, but mixtures of definite compounds. Chemical analysis can teach nothing about the nature of the compounds thus mixed; in order to solve this question, I have proposed to employ the microscopic method which has allowed us to make such great progress in the study of the rocks of the earth's surface. But this method can only be used for crystallized bodies; among the cements and limes, the cements known as Portland, or slow setting, alone fulfill this essential condition; it is with these that I have concerned myself.

Anhydrous Cements.—The examination by the microscope of a thin section cut from a clinker of Portland cement shows immediately two predominating constituents which recur without exception in all the samples. (Fig. 2, facing page 86).

1° *Colorless crystals,* with weak double refraction, with square or hexagonal cross sections and very clear borders much resembling those of the cube. It is by far the most abundant constituent.

2° In the space between these crystals, a ground mass, the color of which is always dark and varies from a yellowish red to a greenish brown. *Its double refraction is stronger than that of the preceding material,* but it does not possess any clear crystalline contours.

3° Beside these two essential elements, accessory elements are frequently found, varying in different samples:

a. Crystalline sections of forms and dimensions analogous to those first given, but which are distinguished from them by a light brownish, slightly yellowish color, a complete absence of transparency, and by very fine striæ inclined to each other about 60°. This constituent, although scarcely plentiful, is found, however, in almost all samples of cement of good quality.

b. Very small crystals of sufficiently energetic double refraction to give polarization colors. This constituent is always in small quantity and is sometimes entirely absent. It is found especially in underburned cements.

c. Certain forms without action upon polarized light and of negative character which do not give any distinguishing test.

This microscopic study, which of itself is insufficient to make known the nature of the crystallized compounds observed, notwithstanding, when it is taken in connection with the absence of fusion of cements during their calcination, reveals this very important fact:

The pseudo-cubic crystals, which are constituents of the first consolidation are not fused, but have formed by chemical precipitation in the midst of the fusible brown material, the constituents of the second consolidation, which after having acted as a flux and made the chemical reactions possible, has solidified by cooling, filling up all the spaces which then remained open.

The action of chemical reagents upon a thin plate of cement placed under the microscope can be studied. I shall successively pass in review the action of the acids, the salts of ammonia, etc.

The acids even when very dilute and weak, like acetic acid, attack all the constituents of cement very rapidly, the destruction can be recognized in polarized light by the

total extinction of the plate. From this it can be concluded that *all the visible compounds contain lime* because silica and the silicates of alumina and iron, the presence of which in a free state in cement is assumed by some authors, are entirely unaffected by weak acids. Upon allowing the plate to dry after being attacked, a white skeleton of silica is seen, not showing any important break in continuity, *the essential elements of cements are therefore all silicious.*

The ammoniacal salts destroy in about a quarter of an hour the pseudo-cubic crystals which constitute the major part of cements, whereas the other constituents of cements active under polarized light only disappear after the end of several hours. If account is taken of the fact that the ammoniacal salts exercise a more energetic action than water attacking, for example, di-calcium silicate, which is not altered in water, we may conclude from this test that the pseudo-cubic crystals, are the only bodies, among those acted upon by polarized light, which play any part during the hardening of cement. Farther on, we shall see the confirmation of this fact in studying hydrated cement.

Ferro- and ferri-cyanides added to hydrochloric acid enable us to recognize the distribution and the degree of oxidation of the iron. The sesquioxide is found in abundance in the colored flux which surrounds crystals of the first consolidation and only there. The protoxide of iron is found in isolated and very rare opaque, slowly attacked grains which are magnetic oxide, arising generally if not exclusively from the emery used to grind the plates. Moreover, this absence of protoxide of iron is confirmed by directly attacking cements by sulphuric acid, and adding permanganate, which in the greater number of cases is not decolorized. The presence of protoxide of iron in cements is only accidental.

There are no characteristics which enable us to recognize the distribution of the alumina, but it is not rash to assume that it occurs with the sesquioxide of iron. This being admitted, one may conclude from this chemical study.

The pseudocubic crystals, the essential constituent of cements, as well as the opaque striated cells, and possibly also the crystals of strong double refraction are composed of silica and lime.

The colored flux which fills the voids left by all these crystals is a multiple silicate of alumina and iron and of lime.

Of these compounds, only the first seems sufficiently alterable to enable it to take any important part during the hardening.

This study teaches nothing of the nature or even the existence of compounds which are not abundant and which would be without action upon polarized light.

It remains to determine the chemical formulas of the crystallized compounds brought out by polarized light.

Numerous attempts to make the proximate analysis of cement clinkers either by reducing the ferruginous parts by hydrogen and separating them by the magnet, or by making use of a mercuric iodide solution, have been unsuccessful. I have thought that by seeking among the cements those which contain the least alumina and iron, one might get an approximate idea of the composition of tri-calcium silicate, the essential constituent of cement. I have succeeded beyond my hopes in this direction. A cement similar to Portland cement is made by grinding "grappiers" or the residue from the slaking of first-class hydraulic limes, which are generally very silicious limes and containing scarcely any alumina.

These grappiers, examined before grinding, are a mixture of very various products, of which half at most is really cement. By a microscopic and chemical examination, I have discovered the following materials:

1° *Fragments of limestone, or unburned fragments;* white, hard grains, effervescing with acids, showing in thin plates the strong double refraction characteristic of calcium carbonate.

2° *Unslaked lime,* white, friable, porous, grains, slaking by a long continuance in the air, it is unslaked lime.

3° *Hydrated and hardened lime,* white friable, porous grains, losing considerable water upon calcination; these are fragments of lime which, instead of slaking, have set because they were too wet.

4° *Wollastonite,* very hard, translucent, almost transparent, grains, coloration active in polarized light; their analysis leads almost exactly to the formula $SiO_2.CaO$ after subtracting from 3 to 4 per cent. of alumina and iron and a corresponding quantity of lime.

The analysis of divers similar samples of different origin have indeed given me the following results:

	SiO_2	CaO	Al_2O_3	Fe_2O_3	H_2O & CO_2	MgO &c.	Molecules of CaO for 1 molecule of SiO_2
Teil	43.0	46	5.5	1.0	0.0	1.0	1.15
Senonches	43.0	45	3.3	1.2	0.7	1.2	1.14
Paviers	45.5	48	4.4	1.4	0.3	0.7	1.14
——	47.0	49	2.0	1.5	0.3	1.0	1.13

The excess of 0.15 of a molecule of lime for one of silica corresponds to the proportion of alumina and iron, which is, on the average, 0.1 molecule. It seems singular at first view that these losses arising from the irregular action of the silicious walls of the furnace and the fuel ashes should show so regular a composition. Samples

ought to be met with containing a greater proportion of lime; if this is not the case, it is because the silicate in the form of di-calcium silicate pulverizes spontaneously and consequently passes totally into the bolted lime.

5° *Grappiers of Cements.*—These are hard grains of saccharoidal fracture, green or grey, showing in their sections crystals identical to those of cements. They are almost exactly joined one to the other, the colored flux being almost absent. (Fig. 1, facing page 86). Their analysis ought therefore to give very exactly that of the crystals in question, and consequently to be identical whatever may be the origin of the grappiers. The following table of analysis shows that this composition differs little from the formula

$$SiO_2.3CaO.$$

The grappiers analysed come from the lime of Teil (Ardèche) Senonches (Eure) and Paviers (Indre-et-Loire).

	Analyses.						Molecules of CaO for 1 molecule of SiO_2
	SiO_2	CaO	Al_2O_3	Fe_2O_3	H_2O& CO_2	MgO SO_3&c.	
GreyGrappiers,Paviers	26.0	66.0	3.0	1.2	1.1	1.0	2.75
——— Teil..........	26.0	66.0	3.5	0.8	1.0	1.0	2.75
Green Grappiers, —..	24.0	69.0	2.7	0.3	1.0	1.0	3.08
—— Senonches......	25.5	68.0	3.6	0.7	0.7	1.3	2.85

The pseudocubic crystals, which are the most abundant and at the same time one of the most alterable constituents of cements, are therefore composed of a calcium silicate differing little from the formula:

$$SiO_2.3CaO.*$$

* The hydraulic limestone of Teil which on the average corresponds almost exactly to this composition, gives by a suitable calcination a cement of the very first quality equal, if not superior, to the best Portland cements. It is an industrial proof of the exactness of the formula which I have assigned to the active element of cements.

I have not been able to establish in even an approximate manner the composition of the multiple silicate which serves as a flux; but I ought to add that the solution of this question only has a secondary interest from the standpoint of the theory of cements, since this slightly alterable compound does not seem to take any part in their hardening.

Among the non-essential elements, I have cited at the head of the list, the opaque, light yellow, finely striated, crystals. However, they do not occur in very calcareous cements; their abundance increases with the proportion of silica, they are especially observed towards the surface of clinkers at points contaminated by the fuel ashes. Their presence has an intimate relation with the spontaneous pulverization of cements. These opaque crystals are only cracked, unorganized crystals, pulverizing spontaneously, a property pertaining to the silicate $SiO_2.2CaO$. All of these characteristics are so concordant that one is tempted to assume the formation of this compound in a pure state, but on the other hand, from microscopic examination the general appearance of these crystals is so similar to those to which I have assigned the formula $SiO_2.3CaO$ that it is very difficult not to assume the continuous passage of one into the other.

It might be supposed that the two silicates $SiO_2.2CaO$ and $SiO_2.3CaO$ form isomorphous mixtures, the pulverization of which is more complete and easy as the proportion of the first of these silicates is greater.

The crystals of sufficiently strong double refraction to give colors in polarized light remind us of wollastonite, $SiO_2.CaO$. They are too rare and moreover resist reagents too strongly to take any part whatever in the hardening of cements.

The crystals which do not act upon polarized light are

those whose study presents the greatest difficulties, since nothing warns us of their presence and no characteristic permits us to recognize their destruction under the influence of reagents. It was natural to seek among these bodies for the presence of lime which crystallizes in the cubic system. Since Rivot, the presence of free lime in cements has been admitted and it often happens that it is attempted to determine it by analysis. In fact, Rivot had recognized the presence of lime only in the hydrated cements, and he had assumed as evident that if the hydrated cements contained lime, it ought to be the same for the calcined cements, an entirely erroneous hypothesis. Quick lime can be very easily recognized, because of its property of slaking, the effect of which can be further exaggerated by using water heated to 100° C. The presence of traces of lime in a cement suffices to cause a very evident swelling and cracking.

The addition of 1 per cent. of lime from the strongly calcined nitrate, to Portland cement of first quality, after pulverization has produced the following results:

The pure cement was made into mortar and then mixed with the lime, using the quantity of water strictly necessary; the briquettes were fashioned in the form of cylinders two centimeters high and two centimeters in diameter, which were, 24 hours after taking set, heated in a water bath at 100° C. during 24 hours.

	Strength.	Increase in bulk.
Pure cement.................	320 Kg.	None
Pure cement 1% CaO......	112	10%

These figures allow cements of good quality to be considered rigorously exempt from free lime.

It is necessary to class certain aluminates among the cubic compounds, and as a consequence, without action

upon polarized light. I have tried to recognize them by using their solubility in water. Finely ground Portland cements agitated with a large excess of water always allows small quantities of alumina to dissolve. This fact, considering the inalterability of the double silicates of alumina and lime seems therefore to establish the existence in the calcined cements, of small quantities of a calcium aluminate.

This solution of the aluminate is much more important in Roman cements. The following figures give the quantity of alumina dissolved from 10 grams of cement from Vassy by ten minutes' agitation in 1 liter of water. The 3 samples came from 3 different factories:

	Al_2O_3 in 1 liter. grams.
Cement A	0.04
Cement B	0.045
Cement C	0.035

To sum up, the absence of free lime in Portland cements of good quality is very certain; the existence of the aluminate is only probable.

This chemical study of the calcined Portland cements shows therefore that they are formed essentially of a calcium silicate differing little from the formula $SiO_2.3CaO$, which is the active element of hardening, and that the compound is produced by chemical precipitation in the midst of a molten double silicate, which has acted as a vehicle for the silica and lime to allow them to combine, but which remains sensibly neutral during their hardening.

Hydrated Cements.—A briquette of Portland cement which has hardened under water for several months shows a clearly crystalline structure under the microscope; small crystals in the form of hexagonal plates are recognized in all the cavities. The surface itself bristles with these

crystals when the hardening has taken place protected from the carbonic acid of the air. Cut into thin sections and examined by polarized light, these cements have sharply illuminated borders showing brilliant colors which very clearly constitute the prolongation of the hexagonal crystals that cover the briquettes. Outside of these isolated borders only a whitish, slightly translucent mass without action on polarized light is seen which shows no apparent indication of crystallization. This negative characteristic has no value; we have seen, indeed, that hydrated plaster formed by the massing of long needles of crystallized gypsum has the same appearance. It is because these crystals are very slender and within the thickness of a thin plate, a great number, oriented in all directions, are superposed.

We will presently see that it is the same with cements. Finally in the midst of this mass, we perceive from place to place outlines of larger grains of cement which are recognizable in the ferruginous flux which preserved them almost unaltered, and which still gives the contour of the crystals of the calcined silicate, which has been entirely transformed.

The hexagonal plates with which the briquettes of cement bristle sometimes attain a size of several millimeters; it is then easy to detach them for examination. The angles of these plates measured by the turning stage of the microscope are very exactly 60°. Two consecutive angles of a similar plate thus measured have been found equal to 59° 52′ and 59° 36′, numbers which differ from 60° by less than 1°, the error possible with the method of measuring used. The double refraction along the hexagonal axis is very weak and irregular, no direction of extinction exists, but perpendicular to its axis the double refrac-

tion is very strong. In converging light the black cross is very clearly observed. These are unaxial negative crystals; their chemical analysis has given the following results:

Weight of material, grams	0.062	0.088	0.243	0.183
CaO	71.0%	0.3%	00.5%	73.6%
H_2O	27.4	23.0	18.5	22.6
SiO_2 (by difference)	1.6	6.7	17.0	3.8
	100.0	100.0	100.0	100.0

It is seen, therefore, that they are calcium hydrate contaminated by a little silicate, the presence of which tends to give, along the axis, a weak double refraction which is entirely absent in pure calcium hydrate. Even the manner in which the crystalline shapes are distributed in the cement mass, their absence of crystalline boundaries shows indeed that the calcium hydrate crystallizes by surrounding and joining all the foreign substances which it contains, just as the calcium carbonate in the calcite of Fontainebleau surrounds the sand in the midst of which it has crystallized.

The relatively considerable dimensions of these crystals when taken in connection with the slight solubility of calcium hydrate, makes it evident that the production of this body is the result of a very slow reaction which could not be the simple hydration of the quick lime. By following the growth of these crystals, it is easily ascertained that it is prolonged through several months.

The amorphous mass which constitutes the most important part of the hardened cements can be studied, as was done with plaster, by following with the microscope the progress of the hardening. Some special precautions are necessary to avoid the decomposition of the hydrated calcium salts, as much by excess of water, as by the carbonic

acid of the air. I take a thin section of cement glued upon an object glass and attach a cover glass without sticking it to it. Then I immerse all in lime-water diluted with its own volume of water, taking care to put the plate of cement underneath. By taking this plate out from time to time and examining it by the microscope, the progress of the hydration is easily followed. At the end of two or three days, wide crystals with strong double refraction are first noticed; they are calcium hydrate. Besides, the cement is often bristling all over with extremely fine needles being scarcely 1-100 of a millimeter long, the subsequent massing of which finally forms the body of cement. (Fig.4, facing page 86). More frequently only fibrous masses are seen to form, resulting from the union of all of these small crystals. The ammoniacal salts instantly destroy these crystals, leaving gelatinous flocks of silica. They are composed of a calcium silicate to which I have assigned the formula of the only hydrated calcium silicate which I have been able to produce synthetically:

$$SiO_2.CaO.2\tfrac{1}{2}H_2O.$$

Lastly, there is formed about the plate at variable distances, small spherolites giving the black cross in paralleled light. The distance at which they are formed is the indication of a certain solubility which reminds one of the aluminate, but this is only a simple hypothesis. The formula should be

$$Al_2O_3.4CaO.12H_2O.*$$

The only aluminate which may be able to exist in the presence of an excess of lime. The formation of hydrated aluminates during the hardening of cements is confirmed, at least in the case of Roman cements, by the study of

* See footnote, p. 67.

their progressive decomposition in the presence of water. Upon shaking some cement from Vassy in the presence of water until complete hydration, and removing half of the water every day, we notice that the strength of the liquor in lime is at first maintained constant and nearly 1.2 grams (per liter) which confirms the existence of free lime in the hydrated cement. Then the strength decreases almost proportionately to the quantity of water added, until it stops at a new stationary strength 0.22 grams (per liter), which corresponds exactly to the decomposition of the aluminate. In one experiment I have observed the following results:

	Lime per liter. grams.
3rd day	0.28
4th day	0.22
5th day	0.22
6th day	0.18

If now we compare the results to which the study of calcined and hydrated cements has led us, we will be led to conclude that *the fundamental reaction which brings about the hardening is the splitting up of a basic calcium silicate into mono-calcium silicate and calcium hydrate:*

$$SiO_2.3CaO + Aq. = SiO_2.CaO.2\frac{1}{2}H_2O + 2Ca(OH)_2$$

a reaction analogous to that which accompanies the setting of di-barium silicate.

There is formed accessorily, a basic calcium aluminate, the rapidity of hydration of which intervenes in the more or less rapid set of different cements:

$$Al_2O_3.3CaO + Ca(OH_2) + Aq. = Al_2O_3.4CaO.12H_2O.$$

this second conclusion being stated only with reserve.

Lastly, iron certainly takes no part in the set of Portland cements; there is no calcium ferrite formed; we

would recognize it immediately by the brown coloration under the influence of carbonic acid, as a result of the liberation of hydrated oxides of iron. It, on the contrary, intervenes very clearly in Roman cements.

I have spoken above repeatedly of the crystallized silicates and aluminates, which are formed either during the calcination or during the set of cements; the figures opposite show the structures observed in their sections, namely:

Figure 1.—A thin section of grey grappier from Teil showing very feebly double refractive crystals of $SiO_2.3CaO$ separated by a small quantity of a ferruginous matrix.

Figure 2.—A thin section of Portland cement from Boulogne showing the same crystals as the grey grappier from Teil, and a much more abundant ferruginous matrix.

Figure 3.—A cement similar to the preceding in which some crystals have become developed in an exceptional degree.

Figure 4.—The beginning of hydration of a Portland cement, showing the elongated crystals of the hydrated silicate, $SiO_2.CaO.2\frac{1}{2}H_2O$. The dimensions of these last have been considerably exaggerated, nearly doubled, in order to give more clearness to the design.

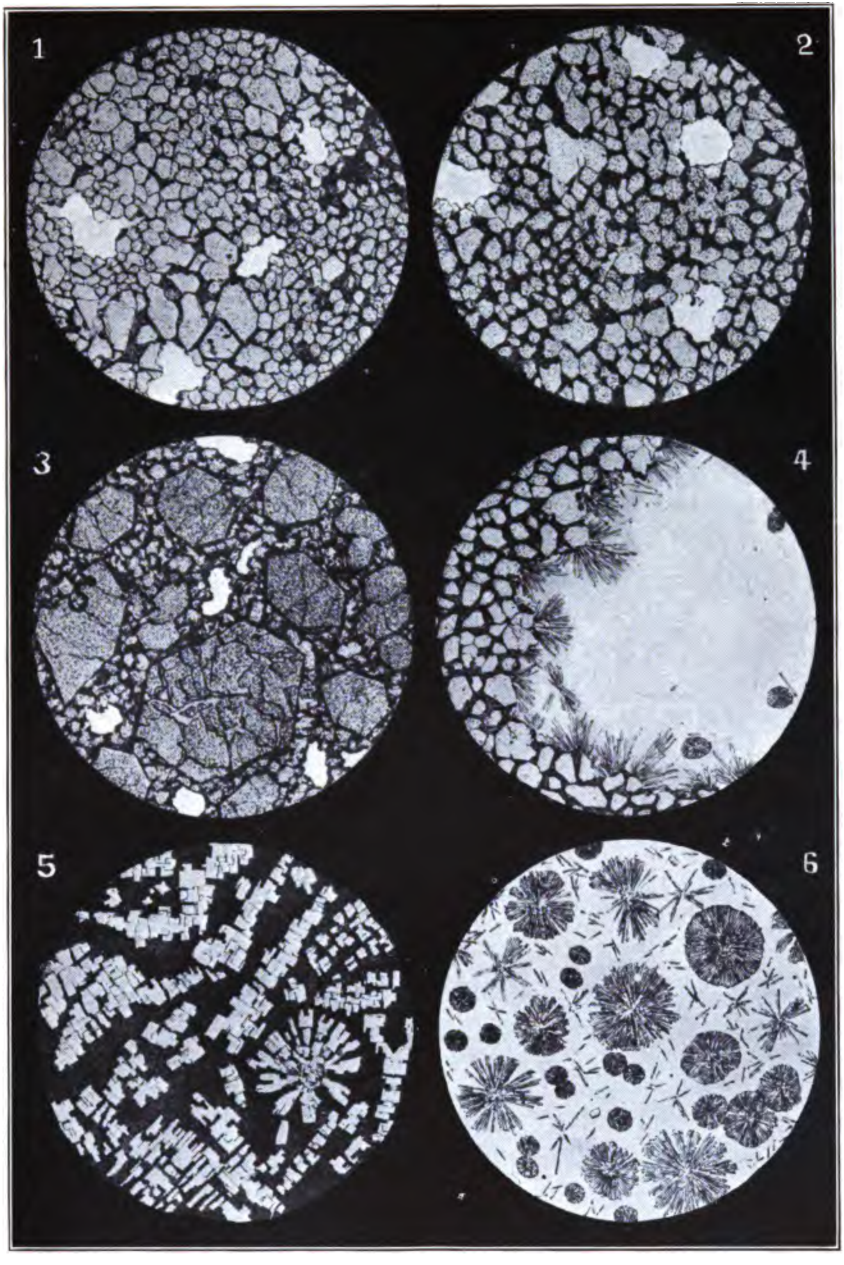
Figure 5.—Crystals of the aluminate $2Al_2O_3.3CaO$ produced synthetically.

Figure 6.—A crystallized precipitate of the hydrated aluminate $Al_2O_3.4CaO.12H_2O$.*

MANUFACTURE AND INDUSTRIAL USE.

From the preceding investigations we are able to deduce certain conclusions relative to the manufacture and the in-

* See footnote, p. 67.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dustrial use of cements. I shall successively treat of the different kinds of hydraulic products:

Portland cements, Roman cements, hydraulic limes and puzzolanas. I shall study their *composition* and their *calcination,* their *hardening,* the *causes of their destruction* and the *methods of testing.*

COMPOSITION AND CALCINATION.

Portland Cements.—It is possible to define rigorously the extreme limits of composition which completely calcined cements, such as Portland cements generally are, can possess. It suffices for this purpose to recall that they must not, on the one hand, contain any free lime which fixes a maximum for the proportion of lime, and that, on the other hand, the presence of too great a proportion of di-calcium silicate leads to spontaneous pulverization upon coming out of the kiln, which fixes the lower limit of the lime content.

1° Upper limit of the quantity of lime. In the presence of increasing quantities of lime, the compounds which tend to form are:

$$SiO_2.3CaO \text{ and } Al_2O_3.3CaO.$$

The silico-aluminates tend to disappear completely; we therefore ought to have as the upper limit of the lime

$$(1)\ \frac{CaO+MgO}{SiO_2+Al_2O_3} \geqq 3.$$

The quantities of each body being expressed in this formula not in weights but in molecules, I have not included iron sesquioxide in the calculation, since calcium ferrites swell in slaking. It therefore is not necessary to combine the oxide of iron with lime.

2° Lower limit for the lime content. Upon diminishing the lime the proportion of silico-aluminate increases, and when that is completely formed, di-calcium silicate $SiO_2.2CaO$ begins to be produced. The formula of the silico-aluminate is not known. We know only that it is at least as calcareous as the most calcareous of those which are known at present, gehlenite $2SiO_2.Al_2O_3.3CaO$. I have assigned this formula to it for the purpose of calculation. We then find as the lower limit of the molecular ratios:

$$(2)\ \frac{CaO+MgO}{SiO_2-(Al_2O_3+Fe_2O_3)} \geqq 3.$$

Here it is not necessary to separate the iron and alumina which act in the same manner with respect to the formation of multiple silicates.*

It is easy to ascertain that the two conditions stated above are satisfied for all the cements of good quality made in France, as the following table shows:

Origin of the Cement.	Formulas. (1)	(2)
Boulogne	2.22	3.6
Desvres	2.28	3.8
Frangey	2.55	4.05
Grenoble	2.4	3.9

* The question whether magnesia should be added to the lime in these formulas and the oxide of iron added to the alumina has been the subject of numerous and tedious discussions, without decisive proofs resulting one way or the other. I must, however, recognize that the rather summary arguments which I have invoked are indeed quite insufficient to settle this question which has not perhaps, after all, had the importance which has often been attached to it. The permissible variation in the composition of cements is, on the one hand, sufficiently large and, on the other hand, the quantity of these two bodies is never great.

On the contrary, for mixtures giving pulverulent cement, I have found:

Boulogne	2.7
Desvres	2.6

And, lastly, for a cement with an excess of lime made at Boulogne for the purpose of experiment and which swelled enormously:

Boulogne	3.2	...

It is seen by these figures that the theoretical predictions are fully confirmed. But it may be asked why the composition of the cement is never represented by formula (1 corresponding to the exclusive production of calcium and aluminum silicates? The lime is always too low. The ratio of bases to acids which ought to be equal to 3 very rarely exceed 2.5. The reason of it is that in the industrial calcination of cements the reactions are never entirely complete in consequence of the lack of fineness and homogeneity in the slurry, and the duration and temperature of the calcination are insufficient. In order to obtain the whole reaction, an increase in cost entirely out of proportion to the improvement of the quality of the product would be involved. It is preferred, in order to avoid the presence of free lime, to increase a little the proportion of the acids, silica and alumina. There is no inconvenience from this excess of acids, except in the formation of a little of the inert silico-aluminate.

In each factory the conditions of homogeneity of the slurry and of the calcination remain sensibly the same. Thence it results that the slurry giving the best product should have a perfectly definite composition for each factory, but will vary from one factory to another with the

conditions of manufacture. This is the explanation for the well known fact which at first seems paradoxical, that in one factory the variations of the proportion of clay in the slurry must not reach 1 per cent., whereas, as between one factory and another the difference may be more considerable.

These narrow limits do not allow the use of natural mixtures of limestone and shale designated under the name of marls or marly limestones. In order to obtain a composition of slurry of suitable homogeneity, it is necessary to make artificial mixtures, the preparation of which becomes an important item of the cost of manufacture. Moreover, the mixture can be made from pure limestones and clay, with each other or with marly limestones; these mixtures may be effected in the dry or wet way, etc. The desired result is equally well obtained by very varied methods, the choice of which depends upon the conditions which prevail at each factory, and with the materials which they have at their disposal.

The mixtures, although intimate, are not and cannot be absolutely homogeneous; the grains of each material, however small, still have finite dimensions. Those of calcium carbonate may reach 1 millimeter. The much finer particles of silica and clay are only several thousandths of a millimeter in diameter, but generally they are grouped in more voluminous bunches.

It is difficult, in spite of all precautions, to avoid the presence of grains of limestone a little too voluminous, which give free lime on burning. It is necessary to slake this lime as much as possible before the use of the cement; for this purpose, the ground cement is left for a certain time in the air, or sometimes materials which will give up water vapor when they are heated are added in the mills

during the grinding, for example, gypsum, or already hydrated cements.*

During the calcination, the first effect of the heat is to decompose the clays and dehydrate them at a temperature in the neighborhood of 600°. This decomposition simultaneous with the dehydration is evidenced by the action of a potash solution and of sulphuric acid, the first of which dissolves silica and the second, alumina more easily than before the calcination. Between 800° and 900° the limestone is decomposed, liberating its carbonic acid and being transformed into quick-lime. From this moment, the elements of the clay begin to react upon the lime, and this reaction becomes more complete as the temperature is higher and its action more prolonged. At the points of contact of the grains of lime and the particles of clay, fusible products are formed which are diffused in opposite directions, becoming more basic on the one hand and more acid on the other. If we break up a nodule of clay, we will have in the centre the elements of clay, infusible silica and alumina. Then the slightly calcareous fused glasses, afterwards a fused mixture of double silicates analagous to slags, with the mono- and di-calcium silicates, all fusible at the temperature of calcination of cements, lastly, the most basic salts, the active constituent of cement, infusible tri-calcium silicate, and fusible calcium aluminates, and in the last place of all, quick-lime. The proportion of these diverse elements varies in a continuous manner with the degree of advancement of the calcination, tending towards a limit dependent only upon the relative proportions of the elements present.

* The usual temperature of a Griffin mill being about 75° C, and of a Davidsen tube mill being about 83°, it is doubtful if gypsum loses any moisture.—Translator.

With a large excess of lime, the final products will be quick-lime, tri-calcium silicate and tri-calcium aluminate. By diminishing the quantity of lime, we would have these two salts and no quick-lime. Afterward the calcium aluminate will disappear and will be replaced by a multiple silicate of a composition analagous to that of the basic slags from blast furnaces.

This will be followed in turn by the disappearance of tri-calcium silicate, which will be replaced by di-calcium silicate with spontaneous pulverization; then by the mono-silicate.

Finally, glasses analogous to the acid slags of blast furnaces will be produced.

In order to obtain calcination, the temperature must be the higher, as the multiple silicate which serves as a flux and allows the diffusion of silica and of lime in opposite directions is itself less fusible. A silicate containing only either alumina or sesquioxide of iron will be less fusible than if these two bases are both present at the same time, and it is possible to conclude from analysis that the maximum fusibility will be obtained with equal equivalents of these two bodies, say in round numbers, half as much again sesquioxide of iron as alumina.

It is seen from this how slurries of variable composition will be able to give similar products by different calcinations; a moderate calcination applied to a slurry low in lime will be able to give, by reason of an incomplete calcination, free lime and calcium aluminate just as a complete calcination applied to a mixture richer in lime will do.

For example, in order to increase the rapidity of the set, an indispensable quality in certain works, the calcination will be produced at a lower temperature to make the reaction less complete and augment the proportion of the

aluminates, but at the same time, the proportion of the lime will be diminished by several per cent. to avoid the possibility of any of it remaining uncombined.

In addition to the normal Portland cement studied above, which comes from the kiln in greenish clinkers with a scorcacious appearance and very hard, there will be taken from the kiln about 25 per cent. of refuse,* or at least mediocre cement, which for reasons of economy has habitually been made to pass with the rest.

These are, first, pulverized materials designated under the name *blue powders* arising from the disintegration of well calcined clinker, but containing too large a proportion of di-calcium silicate. The presence of this silicate is due to excessive burning in the case of a too argillaceous slurry, and likewise to the superficial action of fuel ashes, or of the siliceous walls of the kilns upon (the surfaces of) the clinker. These powders harden slowly, but in the long run may take set with great hardness, like the hydraulic limes. On the other hand, they have the great merit of being certainly exempt from free lime, and consequently are not subject to swelling.

Secondly, unburned slurry is found, brown or grey, and porous, which little by little slakes from the moisture of the air, giving a brown powder. These unburned slurries contain free lime and calcium ferrites and aluminates. After a gradual slaking they give a cement which takes set rapidly, but of slight and very irregular strength.

Lastly are found near the furnace walls, silicious scoriae, glasses and often perfectly crystallized masses of wollastonite $SiO_2.CaO$, inert material which often has been erroneously considered as overburned clinker.

Roman or Quick Setting Cements.—The necessity of

* This refers to the old shaft kilns.—Translator.

preparing the slurry for Portland cement by artificial mixtures considerably increases the cost of production of the latter. The calcination of the natural mixtures constituting the marly limestones, which is much more economical, may be used for the manufacture of cements of ordinary quality, but these differ entirely in their composition, calcination and use, from the Portland cements. Experiment has demonstrated that the best results are obtained by using limestones rich in clay, by burning the rock slightly, and, lastly, by letting the cement slake in the air before using it.*

These cements after calcination appear in the form of brown porous, light, friable masses, having no external appearance of fusion. They seem to contain besides a small quantity of tri-calcium silicate, some free lime and calcium aluminates and ferrites, and at the same time acid silicates, all products resulting from an incomplete reaction. A partial slaking before use is advantageous in order to eliminate the free lime, but too long standing in moist air deadens them completely. This slaking is facilitated by the porosity of slightly calcined cement. Calcium ferrite is easily recognized by the discoloration of mortars during their set, due to the formation of white hydrated calcium ferrite, soon followed by a brown superficial coloration upon contact with the carbonic acid in the air, by reason of the liberation of the hydrated sesquioxide of iron. These cements of inferior quality have only in their favor their low cost of production, due to the use of natural

*All the Roman cements contain a rather high percentage of sulphuric acid. Mr. Candlot has shown the necessity of the presence of this body, without which those cements which have a strong proportion of clay will fall to powder upon cooling. (Comptes rendus de la réunion des membres français de l'association internationale des méthodes d'essais, mai, 1903.)

limestones, to the small quantity of fuel necessary for their calcination, and to the small expenditure of mechanical work necessary for their pulverization.

Hydraulic Limes.—The hydraulic limes are obtained by the calcination of argillaceous, or better, silicious limestones containing less silica and alumina than cement rocks. The proportion of free lime remaining after calcination ought to be sufficient to bring about the complete disintegration of the mass by slaking without employing any mechanical process. For these reasons, the cost of production of limes is much less than that of cements; but, on the contrary, they have the disadvantage of hardening less rapidly and less completely, part of the active constituents having been destroyed during the slaking. A good limestone for hydraulic lime ought to be constituted almost exclusively of silica and calcium carbonate, all the other materials giving compounds which remain inert during the set, either because they are not attacked by water or, on the contrary, being too easily altered like the aluminates, they hydrate during the slaking. Iron and aluminia, however, facilitate the calcination, as they do for cements, making it more economical, by allowing the use of a lower temperature and a less prolonged calcination. From this standpoint only, the presence of small quantities of these materials may be advantageous. In limes of good quality observation shows that the proportion of these does not exceed 3 per cent.

The infusibility of silica and lime is an obstacle to their mutual reaction, which is always very slow and easily remains incomplete. Even in the presence of an excess of lime it is difficult to avoid the formation of insufficiently basic, and inert, silicates. We can hope to obtain a suitable hydraulic lime by the calcination of a silicious limestone

only when the silica present is in a very fine state of division. In the limestone of Teil the silica appears in small spherical grains of less than $\frac{1}{1000}$ of a millimeter in diameter. Limestones containing silica in the state of quartz sand, the grains of which always have an appreciable diameter, cannot be advantageously used, but it is only the size of the grains, and not their crystalline state, as has been maintained, which makes it unsuitable to yield hydraulic products.

The most suitable relative proportions of silica and calcium carbonate in a limestone, taking account of the formula of only the active silicate $SiO_2.3CaO$, will be:

SiO_2	16.6
$CaO.CO_2$	83.4
	100.0

But, indeed, on the one hand, more limestone will be needed to furnish the free lime which by its slaking will permit the spontaneous pulverization of the material, and, on the other, more silica will be necessary, a part of which always escapes from the reaction which remains incomplete. These two requisites practically compensate each other, and observation shows that the limes having the best reputation approach the composition indicated above.

The intensity of the calcination has a great influence upon the quality of lime, a strong calcination rendering the reaction of the silica with the lime more complete, increases the proportion of tri-calcium silicate, and in consequence improves the degree of hydraulicity of the product, but, on the contrary, it diminishes the proportion of free lime, which makes the slaking more difficult. With the slightly silicious limestones containing more than four molecules of lime for one of silica, the calcination can

never be too intense; sufficient free lime will always remain to insure the slaking.

It will be quite the contrary with limestones not containing more than three molecules of lime for one of silica; a very intense calcination gives what is called *black grappiers* of cement, or the limit limes of Vicat. This product is not pulverized by slaking, and can begin to set only when it is finely ground, without previous slaking, but then it relaxes at the end of a certain time, swells, and ends by disintegrating under the influence of the small quantity of free lime which it contains. If the grinding is caused to be followed by a sufficiently prolonged air slaking, in order to make it complete, a hydraulic product of very good quality will be obtained.

As the burning is less complete, a lime which is more easy to slake will result and no grinding will be necessary, but, at the same time, the degree of hydraulicity will continue to decrease. The most suitable degree of calcination will depend upon the means of slaking which is used. The more a factory aims at a careful slaking, the more it will be able to push the calcination toward the production of black grappiers, and the more it will augment the quality of the product. This is the point which sharply differentiates factories calcining similar limestones.

The improvement in quality resulting from the addition of *ground grappiers* to lime is often contested. This difference of opinion comes from the fact that very dissimilar materials are known under the name grappiers. The word grappier designates all those things which escape pulverization by slaking; it is a mixture containing, on the one hand, unburned limestone, badly slaked lime, lime soaked and already set, and wollastonite, all white or yellowish materials and nearly inert, and, on the other

hand, greyish black very hard grains, which are true grains of cement. The proportion of these last vary, according to the nature of the lime and its calcination, from more than 50 per cent. to less than 1 per cent. If in the first case the addition of grappiers is advantageous, it can only be detrimental in the second case.

The slaking has at least as considerable an influence as the calcination has upon the quality of the lime; generally this is the part of the manufacture of limes which leaves the most to be desired.

The slaking, or pulverization, under the influence of a chemical reaction, is a very common phenomenon, produced especially by the action of gaseous bodies upon solid bodies (the spontaneous oxidation of pyrites, the rusting of iron, the hydration of lime by atmospheric moisture). This slaking is the indispensable condition of all reaction between gaseous and solid bodies. If the solid body does not disintegrate, a superficial reaction only is produced, the new compound forms a coating, which prevents the contact, and terminates the reaction (the oxidation of sheets of zinc in the air). The slaking upon contact with liquids is, on the contrary, exceptional, only three examples of it are known: the hydration of lime, of baryta and of strontia; and even in these cases the final division obtained is less perfect. The elevation of temperature which accelerates all chemical reactions makes the slaking more rapid and thus seems to make it more complete, by causing water to react in a vaporous state.

In the slaking of a hydraulic lime, it is necessary to obtain the complete hydration of the lime while altering the silicate as little as possible. This result can only be obtained by working at a very high temperature, which keeps the water employed in the state of vapor. In this

state water has not, so to say, action upon the silicates, which it does not cause to slake, whereas it does cause this rapidly with lime, the aluminates and the ferrites. The required elevation of temperature is furnished by the considerable heat of hydration of lime; all losses of heat ought to be avoided with the greatest care, by giving as great a volume as possible to the pile of lime and protecting it against all causes of external cooling. Even under these conditions the slaking is very slow; for the limes which are strongly hydraulic, it normally lasts a week. But this duration is very variable with the nature of the lime. Those which are slightly hydraulic, either as a result of a lack of insufficient calcination, or as a result of a deficiency of silica, may slake in forty-eight hours: for grappiers, on the contrary, the duration of air slaking, whether before or after grinding, ought to be counted by months.

An insufficiently prolonged slaking gives limes the set of which is very rapid, but in time they swell up and disintegrate. Slaking at too low a temperature gives soaked limes, which, having partially hardened during slaking, are no longer able to harden in use, and which, on the other hand, are frequently insufficiently slaked in the work, as a result of the lowering of the temperature, and swell with time.

The slaking of hydraulic limes is therefore the most delicate part of their manufacture. It is impossible to effect it on the ground at the moment of their use; it always ought to be done at the factory.

Hardening.—The hardening of hydraulic materials is divided into two phases, the *setting* and the *hardening* properly speaking; the distinction of which, from a chemical standpoint, is not very clear, but from the practical

standpoint, these two phases have a special importance sufficiently great to merit a separate study.

The *setting* is perhaps only the beginning of the hardening; it is characterized by a progressive diminution in the fluidity of the mortars: it begins to manifest itself by the persistency of breaks of continuity; the voids produced artificially in the paste, which do not close up again under the influence of gravity or capillarity. From this moment the mortar is no longer good for use. The more quick the set, the more difficult is the workman's task. The set is considered as ended when the mortar paste does not yield under the influence of moderate pressure, such as that of the thumb nail or that of a steel rod loaded with a weight (Vicat needle).

The chemical reactions which accompany the setting may be different from those which continue to occur during the hardening, but it is not always so, in the hydraulic limes, for example, it is impossible to establish such a distinction. With the cements, on the contrary, which have undergone only a little or no slaking, there exists, besides tri-calcium silicate, certain compounds, the hydrating of which becomes complete at the end of a few moments: this is the case with the calcium aluminates and ferrites and quick lime. The thinnest parts of the tri-calcium silicate, the surfaces of the grains, undergo thus a rather prompt hydration. These different chemical reactions may at the beginning give a very rapid course to the hardening and constitute the period of set.

It is easy to foresee the circumstances which may cause the rapidity of the set to vary. They are so numerous, that there is scarcely any of the elements of quality in cements, which may be susceptible to such great irregularities. The fineness of the cement, depending upon the

processes of grinding and bolting, the porosity of the grains of cement calcined rapidly at a low temperature, the notable proportions of aluminates and ferrites, giving quicker and quicker cements. Lack of slaking in the hydraulic limes produce the same effect. The circumstances of their use, the external temperature, and the chemical composition of the waters, are not without considerable influence.

When the progress of the set is followed by means of a thermometer, a more precise method of observation than those which are based upon the study of the increase in hardness, at first a period of inactivity is often noticed during which the temperature does not rise: it seems that the chemical reactions do not begin immediately. Then at the end of some moments the temperature begins to rise abruptly and the set becomes rapid. This peculiarity is very simply called the phenomenon of supersaturation, the existence of which I have noted. So long as solution only occurs the disengagement of heat is very slight or none at all, and the setting does not commence. It is only at the moment when supersaturation by crystallization begins that the setting occurs manifestedly itself by a rapid disengagement of heat.

The *hardening,* properly so called, is occasioned almost exclusively by the slow and progressive hydration of the calcium silicate, which, after having begun during the setting, continues entirely alone.

The quickness with which hardening is completed is not of great interest, only the final hardness is of consequence. It is necessary to study the circumstances which may influence this final strength. This supposes that cements reach a definite hardness which they afterwards keep indefinitely. Often this is not the case: after passing a maximum the strength decreases. There is, therefore, a

third phase in the hardening of cements during which they undergo more or less complete retrogression. For the present, I shall leave to one side this part of the question, and return to it later in the study of the causes of the destruction of mortars.

I have shown at the beginning of this study that the hardness of a hydraulic mortar depended upon two factors, the *cohesion* of the crystallized compounds, which are formed, and their *adherence,* either to each other or to the sand with which they are mixed. There is nothing to be said of cohesion, but it may be interesting to return to adhesion and to study more in detail the considerable modifications which they often undergo by reason of the variations in external circumstances which apparently are most insignificant.

Adhesion depends chiefly:

1st. Upon the *nature* of the bodies in contact and the relative *direction* of the faces in contact, in the case of crystallized bodies.

2d. Upon the *extent* of the surfaces in contact.

The Nature of the Bodies in Contact.—Crystals of the same nature meeting each other as a result of their development are joined to each other more or less completely. If their relative directions are such that the surface of contact determines two reticular superposable planes, they will be able to unite in such a manner as to form only a single individual. In this case, their adhesion will become equal to their internal cohesion, but, in general, this is not the case, and it is observed that the adherence of two individuals united in any manner whatever is considerably lower than their cohesion. This fact can be shown by allowing to crystallize by cooling, the solution of a salt chosen from among those which do not have easy cleavages,

and by breaking by hand the groups of crystals obtained. It is observed that the force necessary is less than that required to break an isolated crystal and, further, that the fractured surface shows plane faces, indicating that the fracture is produced along the faces of contact of the crystals and not across them, the rupture of which would have produced an irregular surface.

When a foreign inert body is added to one which sets by itself, sand, for example, in order to increase the volume of mortar obtained, account should be taken of the adherence of the crystallized salt with the foreign body.

This adherence depends upon the *chemical nature* of the bodies present, and the *condition of the surfaces.*

Daily laboratory experience shows that salts crystallizing in a glass flask adhere more or less strongly to the walls.

Some allow themselves to be broken rather than be detached. I will cite, for example, the crystals of barium silicate, which are formed in a flask of baryta water; others, on the contrary, are detached under the influence of their own weight; this is the case with calcium sulphate.

I have ascertained that this last salt had no greater adherence to carbonate of lime and quartz, that is, to the constituents of ordinary sand. The addition of sand can, therefore, only diminish the tensile strength of plaster mortars. The grains not joining with the calcium sulphate produce simply surfaces of contact, diminishing the full section almost as air bubbles would. This conclusion is fully in accord with practical results: plaster is always used without the addition of sand. The state of the surfaces also plays a very great part in the adherence. We know that in order to make lime mortar, the sharpest sands give by far the best results. The influence of the sharpness results, first, from the increase of the surfaces of

contact; it is indeed evident that the development of the real surface of a piece of roughened glass is much greater than that of a piece which has been polished, but the principal cause of this influence of roughness, it seems to me, should be searched for elsewhere. We observe, when we attempt to stick any object whatever upon a plate of polished glass with gutta percha or canada balsam, bodies which adhere strongly to glass, that the peeling off, when once begun at a point extends afterward under the influence of a very slight force, and that this does not occur if the glass is roughened. This phenomenon, it seems to me, is related to the facility with which fissures are propagated in a homogeneous and very strong body, such as the glasses, which, once cracked, split completely under a very moderate force, which does not happen with bodies the fracture of which is rough.

Extent of the Surfaces of Contact.—I have said that the second factor upon which the strength of a mortar depends is the extent of the surfaces of contact of these diverse elements. This extent varies with the *form of the crystals,* with the *volume of the voids* remaining in the mortar after the complete set and with the *manner of distribution* of the voids.

Form of the Crystals.—A very weak adherence, per unit of surface, if it is multiplied by a considerable extent of surface, will give as the result a very great total force of adherence, which may even equal the internal cohesion of the crystals, that is to say, the maximum strength which the mortar may be able to show. The surface of the crystals increase, moreover, in proportion as they are more elongated, as they differ more from a spherical form, the surface of which is a minimum. The form of elongated prisms which I have discovered in the crystallization of

plaster and all similar products is, therefore, eminently favorable to the development of adherence.

Volume of Voids.—The quantity of water which it is necessary to use for mixing up a mortar to suitable consistency is generally greater than that which may become fixed by the setting. In order to mix up the plaster as stiff as possible, the quantity of water necessary is about 30 per cent. of its weight, whereas the quantity of water which it fixes is only 15 per cent. Therefore, at least twice as much water is used, and generally still more water is put in in order to slow the set and facilitate the use of the mortar. This water in excess remains imprisoned and forms breaks of continuity which diminish the extent of the surface in contact. If these voids did not exist the crystals would touch each other on all their surfaces and the adherence would be a maximum.

In proportion as the volume of the voids increases, the extent of the surfaces of contact diminishes up to the point when the crystals no longer touch, then there is no setting at all: there is simply a mass of mud formed by the more or less complete suspension of a precipitate in the midst of the excess of water. The volume of voids sufficing to prevent the contact of the crystals, and, as a result, the quantity of water which a mortar can stand without ceasing to set, depends essentially upon the form of the crystals. Elongated prisms will be able to stand a much greater excess of water without failing to touch each other than would be the case with cubes.

We will assume, cubes which may be regularly distributed in space, and the centers of which, for example, form a cubic network, but which may be oriented around their centers in any manner whatever. The requisite condition that they may no longer touch two and two is that their

greatest length, that is, their diagonal, shall be at most equal to the side of the cubic network. The volume of voids, which is easily calculated, will be then a little less than twice the volume of the crystals.

With elongated crystals whose length would be, for example, equal to ten times their width, which, like the cubes preceding, would have their centers upon a cubic network and which would be united in any manner whatever, the contacts would become impossible when their greatest length, that is, their axis, is equal to the side of the cubic network. The volume of voids will then be 99 times that of the crystals, that is to say, that the prismatic crystals ten times as long as they are wide, will be able to stand an excess of water 50 times greater than cubic crystals before completely failing to set.

The evident conclusion of these considerations is that the set of mortar, which always contains an excess of water, can only result from the formation of much elongated crystals: this, indeed, the result to which the direct observation of the facts leads, as I have shown above, aside from all theoretical ideas.

Distribution of the Voids.—In what precedes, I have assumed the crystals uniformly distributed and consequently the voids also. In reality, this cannot be the case: in some places the crystals will be more compacted, elsewhere they will be spaced further apart. This unequal division may have a very great importance in regard to the positive strength. We will take the preceding example of cubes, regularly distributed in space and not touching each other: that is, for which the ratio of voids to filled spaces is equal to two and which, consequently, forms a system of no strength. If we shall modify their distribution in such a way as to place some besides the others

along certain directions, for example, following the faces of a cube bounding a certain volume, we will be able to form a solid collection. It is easily ascertained that the tensile strength of such a system will be half of that which it would have if there had been no voids, that is, half of its maximum value.

I have assumed here that the spacing of the crystals is according to a definite law, an hypothesis which at first view may seem very far from the reality, in fact, similar spacings are produced spontaneously in a very great number of cases, and contribute to notably increase the strength of mortars. We will take a mortar formed of a mixture of finely pulverized cement, as is the custom, and ordinary sand, that is, rather coarse. The grains of sand, more or less rounded, touch each other in certain points, around which the interval which separates these grains increases progressively. It is conceivable that if all the cement can be concentrated in a restricted zone which surrounds the points of contact, the useful effect of a given quantity of cement will reach its maximum. If, on the contrary, the cement is uniformly distributed in all the voids left by the grains of sand, it is very evident that the crystals formed drowned in a great excess of water and for the most part removed some distance from the grains of sand, they will be in much less favorable a condition for strength.

Now this concentration of cement at desired points may be very simply obtained by the capillarity of the water. It is sufficient to let the mortar drain, the most voluminous voids are emptied and the water lodges in the narrower spaces, carrying with it the pulverized cement which collects at the desired points. We know, indeed, that the strength of test briquettes of cement is doubled when they

are put to drain on a porous surface of dry plaster as soon as moulded.

To an analogous grouping of crystals we must, without doubt, assign the increase of strength which plaster takes upon desiccation. The increase of strength thus produced is notable, and it is the greater as the excess of water used for mixing has been greater. Cylinders of dry plaster, afterwards soaked in a saturated solution of calcium sulphate, have given me the following figures on breaking:

	Strength per square centimeter. Kilograms.
Dry cylinders	56
	62
Wet cylinders	28
	30

The decrease in strength has therefore been exactly half. It might be supposed that the process of the phenomenon is analogous to that of the hardening of the clay by desiccation, but in the case of plaster the effect is less marked because the crystals being already joined to each other do not have the entire mobility of the particles of clay. They are only able under the influence of the capillary forces developed by the evaporation of the water to be deflected in the interval between their points of contact in such a way as to come into touch with each other and to adhere to each other at new points. This movement will always be produced in the direction in which the crystals are closer and consequently will diminish the number of breaks of continuity of the mass by increasing, on the other hand, the volume of those which remain; these are the most favorable conditions for the increase of strength. The shrinking of the mass is very slight because it is of the order of magnitude of the approach of two ends of a straight line which is slightly bent: it cannot be com-

parable to that of clay in which every particle approaches the other.

We see, therefore, in summing up, that the magnitude of the adhesive force, and consequently the strength of mortar, are intimately bound up with the elongated form of crystals and their manner of distribution, conditions which themselves depend upon phenomenon of supersaturation.

The elongation of crystals is the greater as they are precipitated in a more strongly supersaturated solution: fineness of grinding, which increases the extent surfaces of solution will therefore be favorable to hardening. This influence of the rapidity of chemical reactions makes itself particularly felt with plaster. We know that the latter when strongly calcined only gives a very mediocre mortar; natural anhydrite does not harden at all. This is not, as is commonly believed, a result of lack of hydration. The water is active, its action is only very slow and the hydrate formed is found in large short crystals which adhere to each other very poorly. This explanation is confirmed by the fact that the crystallized hydrate $SO_3.CaO,\frac{1}{2}H_2O$, which does not differ from calcined plaster, sets very poorly. The absence of porosity and the extent of surface of contact with the water suffice to modify the conditions of the crystallization. Roman cements, calcined at very low temperatures owe, doubtless, to their porosity, and consequently to the rapidity of their hydration, their ability of acquiring a certain hardness, which would not properly be expected from incompletely calcined products, in which the proportion of active material ought to be relatively small.

Raising the temperature, which accelerates chemical reactions, ought to be favorable to the hardening of cements, but experience seems to indicate that between 0° C. and

100° C. the final hardness of products of good quality changes little. Merely the limit is reached much more quickly. It is possible that the temperature might have a special influence upon the elongation of the crystals in a contrary direction to that which produces an increase from the supersaturation. It will be understood that I leave out of consideration the products of poor quality insufficiently slaked, the destruction of which is thus increased, as I shall treat it farther on.

But these are not the only causes which influence the development of crystals: the presence of small quantities of foreign substances in the mixing water may have a very considerable action. I shall recall, in connection with this subject, the experiments of Le Blanc upon the crystallization of alum; but our knowledge upon this subject is too incomplete to enable any application of it to an actual case to be attempted. The existence of such influences seems to be well shown by the difference of results obtained by mixing up a cement with rain water, river water, or selenitic water.

In regard to the way the last circumstance may be able to influence the development of crystals, I will point out the number of centres of crystallization produced in a supersaturated liquid; the fewer of them it has, the more the crystals will be elongated, the more favorable the conditions will be. But it is rather difficult to foresee the circumstances which determine the development of the first crystals. Doubtless in this direction must be sought the cause of the bad results obtained with dead cements. Hydration by the air of only several per cent. of the active elements deprives a cement of all of its qualities. There seems to be no proportionality between cause and effect. The final strength ought to diminish several per cent. if

the hydrated parts behave like inert materials. By creating an infinite number of centres of crystallization on the surface of all the grains, they ought to oppose themselves to a suitable supersaturation of the solution.

CAUSES OF DESTRUCTION OF HYDRAULIC MORTARS.

After having studied the causes of hardening of hydraulic mortars, it is interesting to review the circumstances which may cause their destruction. These mortars may be used in three essentially different conditions:

In free air,
Under ordinary water,
Under sea water.*

Their destruction in these different conditions may be connected with four chief causes: The destruction of certain hydrates by *efflorescence* under the influence of heat

* The study of the decomposition of cements by the sea has made very great progress in these latter years.

Vicat has shown that of the salts of sea water magnesium sulphate alone exerted a really harmful action.

M. Candlot has shown that magnesium sulphate only exerts its action after having been transformed into calcium sulphate and that the destructive action of sea water ought to be charged principally to this body and to its combining with calcium aluminate.

Mr. Maynard made evident the very important fact that contrary to what would be supposed the penetration of the salts of sea water does not take place to the interior of mortars, if I may say so. Analyses of mortars long since immersed do not indicate the presence in the mass of notable quantities of sulphuric acid nor of magnesia, as long as the decomposition is not very far advanced. Nevertheless, the mortar constantly loses lime until all hardness disappears, even when, because of its small content of alumina, it is not the seat of any swelling.

I have verified the accuracy of these two apparently contradictory facts, of the elimination of lime without the precipitation of magnesia. It is very easy to follow the progress of the phenomenon by using, instead of magnesium salts, salts of colored oxides; of silver, mercury, cobalt and copper. At the surface a less and less per-

and dryness; hydration accompanied by *slaking* of certain ultrabasic products; the decomposition of the lime salts by *solution* of their lime, and, lastly, the *decomposition* of these same salts by salts of magnesia.

These different influences will be made unequally sensitive, depending upon compactness of the mortar; consequently, their action will vary with the proportions of

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meable crust of colored oxide, is formed, producing a semi-permeable partition. Lime is diffused from the interior of the mortar toward this surface, where it meets the soluble salt, and decomposes a new quantity of it, which reinforces the superficial crust. On breaking briquettes, after several months' immersion in like solutions, it is recognized without difficulty from the absence of color that no penetration of the colored oxide had taken place. When the salt is a chloride or nitrate, the reaction with the lime solution, but without penetration of the oxide, is continued indefinitely without any apparent alteration of the briquettes. When, on the contrary, the salt is a sulphate of copper or of cobalt (used as a concentration of 6 grams per liter), the effects are exactly the same as with magnesium sulphate used at the same concentration. That is to say, that at first a colored crust is formed at the surface, as with the chloride, but this crust swells up, cracks and reforms anew, and at the end of a certain time the briquettes are seen to split, to swell and to break to pieces completely. It seems that this expansive crust may have a force sufficient to break the cement to which it adheres.

This expansive action of calcium sulphate is difficult to explain. I have discovered, in the first place, that in the formation of calcium sulpho-aluminate there is no increase of absolute volume. The combination of the bodies present is, on the contrary, accompanied by a contraction. Moreover, exactly the same thing occurs in the slaking of lime. The volume of the calcium hydrate is less than that of the quick lime and of the water which enters into its composition. The swelling is the result of an increase of apparent volume. The solid elements repel each other by an unknown means. However it may be, it suffices that these forces of unknown origin may have sufficient magnitude to give the explanation of the destruction of mortars. This is indeed the case from the slaking of lime which develops enormous force. We know that a small grain of lime in the middle of a brick suffices to cause it to crack.

But it is entirely different with calcium sulpho-aluminate. The forces which accompany its formation are extraordinarily weak. They are not sufficient to crack a thin glass or test tube, and yet with time they succeed in dislocating extremely strong masonries. The reason for this paradoxical fact is a consequence of the general

sand and water employed for the mixing. A mortar without voids can be attacked only superficially by fresh or salt water: it will resist much longer than a permeable mortar. The difference will be the same as that which is observed in the solution of a crystal of sugar, or of a piece of lump sugar. The porosity, on the other hand, will retard destruction by slaking, by allowing the swelling to fill up the internal voids before making its action felt outwardly.

I do not think it useful to dwell longer on these facts, which to-day are well known. These being assumed, we will rapidly review the different causes of the destruction of mortars stated above.

Dehydration by Dry Air.—A certain number of hydrated salts, e.g., sodium carbonate, lose their water in dry air, and at the same time disintegrate and are finally reduced to a white powder having no cohesion. Among the

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theory of the rule which I have given. All force acting upon a solid body in contact with an uncompressed liquid increases the fusibility or the solubility of the body considered, which melts and gives a supersaturated liquid in comparison with the same solid uncompressed body. The liquid will then allow the uncompressed crystals to crystallize in the voids and will thus cease to be saturated with respect to the compressed body, which will be dissolved anew, and thus repeatedly, as long as the forces act upon the solid parts of the mass. A porous moist mortar submitted to a continuous stress will be deformed indefinitely until rupture occurs, no matter how weak the stress may be. The quickness of the deformation will change only with the magnitude of this force. The accuracy of this theory is very easily verified by taking a stick of plaster 5 mm. thick, and 250 mm. long, carried on two supports and loaded at its middle point with a weight equal to one-fourth of the breaking stress. It is done comparatively on two similar rods, one dry and the other immersed in a saturated solution of calcium sulphate. The first is not bent; the second bends progressively until it is bent several centimeters and finally breaks. The continued expansive action of calcium sulpho-aluminate suffices to produce like effects, but this action often takes many years to reach its limit, because of the weakness of the stress put into play.

hydrated lime salts produced during the set of cement the calcium aluminates are the only ones which to me have seemed susceptible of meeting with a similar alteration. This cause of destruction is very clear with Roman cements: briquettes left for six months to set under water and afterwards placed in a dry atmosphere are cracked by shrinking. After drying out, heating them for some minutes at 100° is sufficient to cause them to lose half of their strength. Nothing similar is observed with Portland cements of good quality.

The hydration by moist air or even by water followed by swelling is by far the most frequent cause of the destruction of mortars. The presence of foreign substances susceptible to slacking; ultra basic calcium aluminate, magnesian lime or even pure lime, may result from an excess of calcium carbonate in the mixtures submitted to calcination, from an insufficient calcination, or, lastly, from a lack of slaking in the hydraulic limes. This effect is more marked as the grains of cement are more voluminous: the interior escapes the action of the water during the hardening, as I have explained in connection with the action of water upon the aluminates, and can ultimately be slaked upon contact with atmospheric moisture. This cause of destruction is more formidable in the air than in water: certain compounds susceptible of taking set upon contact with liquid water are slaked, on the contrary, under the action of moist air. But if the final swelling is greater in the air, it is, on the contrary, much more slowly produced.

I will cite, as an example, a cement rather rich in lime coming from one of the most noted French factories, which, after six months of setting under water, had given perfectly intact briquettes and showing good strength. These

briquettes, removed from the water, and left in the air, began to crack at the end of three years, and the sixth year were completely disintegrated and reduced to the state of a sandy mass. The finest powder, separated by bolting is shown to be richer in lime than the larger fragments. The disintegration, therefore, is very certainly due to the slaking of a small quantity of free lime.

This different action of water in the liquid or in the vaporous state can be made evident with the greatest ease by experimenting upon salts which are rapidly hydrated, as sodium carbonate, when fused and finely ground and then mixed up with liquid water they take set quickly without slaking; on the contrary, when left in the air, they hydrate slowly and swell enormously. Upon enclosing them in tubes, or simply in paper bags, the envelope is soon seen to burst on all sides, and the salt seen to come out through the crevices.

In order that the slaking of lime may produce such disastrous effects, it is necessary that its slaking shall be very slow, and not become complete until after the hardening of the mortar. The lime obtained by the calcination of pure limestone is an extremely porous mass, which is slaked in a few seconds: in this state it is scarcely harmful, because its hydration is ended before the beginning of hardening, properly speaking. This is what seems to happen with Roman cements calcined at very low temperatures and very porous; but if the lime is compact and does not have pores possessing an extremely considerable surface of attack by the water, the hydration becomes very slow. This compactness is obtained every time that the lime is produced in contact with molten bodies, which dissolve it and allow it to crystallize. Thus this occurs in the decomposition of calcium nitrate, in the calcination of

lime from the carbonate in contact with fusible substances, such as calcium chloride, the calcium aluminates, and calcium sulphate. The retardation is still more considerable when the lime crystallizes in the presence of magnesia, with which it is intimately mixed, either by chemical combination or as an isomorphous mixture. In these cases, as I have shown above, the slaking will take years. There is no other cause to be sought for in the bad results obtained with magnesia cements, it is useless to attribute a characteristic action to magnesia. The substitution of magnesia for lime, molecule for molecule in a cement, has only one result, that of weakening the action of the water, if indeed for a certain magnesia content it would not have taken set at all. A cement capable of taking set can only be obtained by raising considerably the proportions of the bases. Then lime and magnesia remain in excess, which may take set like calcined dolomite, but likewise are disintegrated in time.

The proportion of free lime necessary to alter in a notable manner the qualities of a cement is extremely slight. I have shown above that the addition of 1 per cent. of lime from the nitrate to a cement of good quality suffices to reduce its strength by half.

This cause of destruction seems to me to deserve much greater attention than is usually given to it. I would be induced to believe that at least nine times in ten it is the only cause of the disintegration of hydraulic mortars used in the air or in fresh water. If it escapes observation frequently, it is because its action often does not become sensible until the end of several months, that is, long after the end of the tests which are usually made at present.

The dissolving action of water would cause, with time, the total decomposition of hydraulic mortars, if the car-

bonation which is produced simultaneously did not protect them against this influence. This carbonation is more or less efficient, according to the slowness with which it has occurred. When produced rapidly with the mortars of hydraulic limes, which contain pulverized slaked lime, the precipitate of calcium carbonate will be equally pulverized, without adherence, and will be carried along where water has a passage through the fissures of the masonry. These, instead of choking up, continue to increase. On the contrary, with the cements, in which the free lime is less abundant and especially less finely divided, the slower reaction will cause the adherent crystallization of calcium carbonate, and this will end by filling up the fissures in the masonry, which will thus be produced by the dissolving action of water. A laboratory experiment which I have cited above makes very clearly evident these two different modes of carbonation. If calcium silicate or aluminate is left under water, we see forming gradually, under the influence of the carbonic acid of the air, crystals of calcite adhering to the walls of the flask. If the aluminate or silicate is replaced by slaked lime, there will be formed only at the surface of the liquids crusts of calcium carbonate, which gradually fall to the bottom of the liquid without acquiring any adherence with each other or with the walls of the flask.

It, therefore, is only by virtue of the slow carbonation of the lime that the hydraulic mortars can escape the destructive action of water and resist it in those places where plaster, calcium sulphate, which cannot carbonate itself, is finally entirely dissolved.

The magnesian salts of sea water produce an action analagous to that of pure water, but much more energetic. They dissolve lime, as Vicat has shown, by allowing hy-

drated flocculent magnesia to precipitate. A liter of sea water which contains 2 grams of magnesia can dissolve 2.8 grams of lime, whereas pure water can liberate only 0.052 grams per liter from the silicate. It seems that the magnesia, on being precipitated, ought to crystallize, and consequently to play the same part as calcium carbonate. This doubtless would happen if the precipitation were infinitely slow, but having regard to the slight solubility of magnesia, to the concentration of sea waters in salts of magnesia, and to the concentration in lime of the waters of saturation of the mortar, the reaction is infinitely too rapid to give this result.

With so great a dissolving power of sea water upon cement, the attack would be as rapid and complete as it is for a mortar of plaster placed in running water, if the progressive carbonation of the lime did not come in to protect it against the action of the magnesian salts. It is not necessary to search elsewhere for the cause of the more or less prolonged resistance of cements to the destructive action of the sea. It is, therefore, interesting to study all the circumstances which may favor the formation and the crystallization of carbonates.

The crystallization is the more perfect as the carbonation is effected upon the less soluble lime compounds. It, therefore, seems that the more or less complete elimination of calcium hydrate would be favorable: the addition of a certain quantity of puzzolana to the cement would allow this result to be reached. The use, like sand, of calcium silicates, inert to the action of water, but capable of being attacked by carbonic acid, as the slags of blast furnace are, it also seems ought to be recommended. I have shown that these compounds set perfectly in water charged with carbonic acid. Doubtless they would not be altered by salts

of magnesia. But the best way to assist the carbonation would be to furnish the cement with carbonic acid in greater proportion than sea water can, the content of carbonic acid of which is only 50 liters per cubic meter. The use of alkali carbonates is very costly, it may be that it would be possible to utilize the decomposition of certain organic substances by the lime of the cement, wood sawdust, for example, either natural or transformed into hydrocellulose to make it more easily decomposed. We know, indeed, that all organic substances heated with lime break up in such a manner that all their oxygen passes off in the condition of carbonic acid: at ordinary temperatures the reaction is still produced, but much more slowly. A similar proceeding would allow carbonation to the center of a piece of masonry to occur, and would protect it against all infiltration. Such a method was employed, intentionally or otherwise, by the Romans in the preparation of coatings of fat lime for their frescoes. I have recognized, upon samples brought from Pompeii, that they mixed with the lower layer of the coating a great quantity of fragments of chaff, of which only the casts remain to-day. The organic matter has been completely destroyed in giving the carbonic acid which has aided the carbonation of the lime and which is now complete.

I do not express these ideas as theoretical consequences of the chemical researches mentioned above; they should not be accepted until they have been submitted to the direct control of experiment.

I have not spoken so far of the carbonation of the magnesia precipitated in the pores of a cement; it ought to be produced in the same time as that of lime, and even give place to a more complete crystallization, because of the greater solubility of the bicarbonate. Moreover, mag-

nesium carbonate crystallizes with a certain quantity of water, a favorable condition for the obstruction of the pores of masonry, but the hydrates of this carbonate stable at different temperatures are not the same, and it might be that the crystals at first formed may be afterwards destroyed by disintegrating as a result of variations of temperature: this is a question which would deserve to be studied.

I have not spoken of the hydration of calcium carbonate, because this salt is ordinarily produced anhydrous, and, once formed, it cannot combine with water at any temperature: it is indefinitely stable. However, a hydrate of this salt exists, $CaO.CO_2.5H_2O$, which can be produced by the carbonation of lime below 5° C.; but it is very unstable, and the least rise of temperature transforms it into pulverulent anhydrous calcium carbonate, devoid, consequently, of all strength. It may be useful to take account of this fact, in the hardening of cements at low temperatures, especially for experimental briquettes, exposed to the air or placed under a thin layer of water.

TESTING OF THE HYDRAULIC PRODUCTS.

In concluding this study, I will broach a question which has great interest from a practical point of view, that of the testing of hydraulic materials. It may be asked at the very first if their quality depends upon certain very definite conditions, and, in the second place, if characteristics exist which will allow us to discover, before all, in what measure these conditions are fulfilled. The reply to the first question is evidently in the affirmative; I have shown that a cement of good quality has a perfectly definite composition, and the reciprocal ought to be assumed: all cement

showing this composition will be able to give a cement of good quality when ground and afterwards mixed under suitable conditions, but the means of controlling this condition of composition are absolutely lacking. Rough chemical analysis teaches nothing of the nature of the compounds formed; it does not distinguish between a mixture of silica and lime, a silicate of lime, a cement simply decarbonated which cannot set, and a true cement properly calcined.

The only useful information which may be drawn from the chemical analysis is whether the cement does not contain an excess of bases, that is, more than three molecules of protoxides ($CaO.MgO$), for one molecule of the acids ($Al_2O_3.SiO_2$); the theory that I have given above shows, indeed, that with this proportion of base, it will not contain free lime if the mixture was perfectly homogeneous, but only compounds capable of taking set $SiO_2.3CaO$ and $Al_2O_3.3CaO$.

However, the mixture and the calcination never being perfect, it is preferable to take it a little below this limit. In the calcination, it is not necessary to allow for oxide of iron, since the ferrites are slaked like lime. It is necessary, on the other hand, to deduct from the protoxides the quantity required to saturate the sulphuric acid, and the chlorine, that is, to bring into the analyses, not sulphuric acid, but calcium sulphate, and likewise for the chlorine. These conclusions are fully in accord with the practical results of the cement industry. I will give below the analysis of two cement clinkers: the first of good quality, the second setting with difficulty and soon disintegrating by swelling, as the result of the presence of an excess of lime. The calcination in both cases was complete. I will express the results of these analyses in molecular ratios, silica

being taken as unity, as I have previously done, which makes the comparisons much more easy:

	Normal Cement.		Cement with excess of lime.	
Losses and sundries	0.94%		1.82%	
SiO_2	1.00	1.21	1.00	1.17
Al_2O_3	0.21		0.17	
Fe_2O_3	0.04		0.03	
CaO	3.29	3.37	3.71	3.76
MgO	0.08		0.05	
$CaO.SO_3$	0.015		0.01	
$\frac{\text{Acids}}{\text{Bases}}$	= 2.78		= 3.2	

This table, calculated into percentages,* gives:

	Normal Cement.	Cement with an excess of lime.
Losses and sundries	0.94%	1.820%
Silica, SiO_2	21.43	20.085
Alumina, Al_2O_3	7.66	5.814
Ferric oxide, Fe_2O_3	2.29	1.607
Magnesia, MgO	1.15	0.677
Lime, CaO	65.80	69.545
Calcium sulphate, $CaSO_4$	0.73	0.456
Total	100.00	100.004

The *ultimate* analysis of a cement can thus only indicate a limit of composition, beyond which all the products obtained are certainly bad. The *proximate* analysis, if it were possible, would be able to throw some light upon the qualities of a cement. Rivot had proposed, in this direction, to estimate the free lime by the dissolving action of water; this test is still made in many laboratories. In reality, it has no value, since calcined cements, as I have shown, do not contain free lime. That which is thus obtained comes from the decomposition of the basic silicate, a very incomplete decomposition in forty-eight hours, since the com-

* Using Stas' numbers, as given in Tomassi's Electro-Chemistry, 1889.

plete hydration requires months, so that in this method very little is measured but the rapidity of attack, that is, the degree of fineness of the cement.

I have tried, without success, different methods of proximate analysis, more or less indirect: the action of ammonium salts; the calorimetric measurement of the heat of solution in acids; the microscopic examination of thin sections, but by none of these methods have I succeeded in obtaining conclusive results.

If it is impossible to verify the conditions of composition, it can be attempted without being biased by the composition, to discover whether the cement after hardening fulfills the desired conditions of solidity. These mechanical tests to-day are in great favor, although, indeed, they may be scarcely more instructive than the chemical analysis.

The analogous tests made upon the metals are, it is true, excellent, because they measure directly the conditions of elongation and of strength which define the quality of the metal. This quality, after use, will remain constant as long as a foreign cause does not act to destroy or alter the metal.

For cements, the problem is entirely different; indeed, from the moment of their taking set, they experience a slow evolution which may require years before reaching its limit. This limit only is it interesting to know, and the tests which may require to be made on short notice can teach us nothing of our subject. They give only the tangent at the origin of a curve of which we would want to know the asymptote at infinity, and there is no relation between these two extremities of the curve, which are generally separated by a maximum of variable importance.

Certain very basic cements, magnesian or not, which

give very good strengths during the tests, end after several years by being completely disintegrated; the asymptote then blends with the axis of the coördinates. I will refer here to some examples borrowed from the interesting work of M. Candlot upon Portland cement. The numbers of the table give the tensile strength in kilograms of briquettes of 16 square centimeters cross-section:

	7 Days.	1 Month.	3 Months.	6 Months.
(1) Cement with excess of lime....	350	650	606	506
(2) Cement incompletely calcined...	568	712	609	412
(3) Lumpy powders of cement....	295	410	510	560

We see that the tests at one month, the only ones really practicable, give an enormous superiority to cements containing free lime, which, however, are so dangerous in use: the lumpy powders, coming from the spontaneous pulverization of slightly calcareous cements, the set of which is slow, but which with time acquire very great hardness, would be placed far behind.

In my opinion, the mechanical tests ought to be managed differently. It would be necessary to conduct them in such a way as to bring into relief the causes of destruction, by exaggerating these latter by every possible means. The raising of the temperature allows the desired results to be easily obtained. The strengths obtained at higher temperatures are certainly not equal to those which have been obtained at ordinary temperatures by a more prolonged hardening, but, nevertheless, they seem to classify the different products in an order comparable to that which will be obtained by the tests at normal temperature, which are prolonged a very long time. In every case, this method of testing of hydraulic materials seems to give results more in accordance with the real facts than that which is

habitually employed. I will give, as an example, a series of experiments which I have made comparatively upon the lime of Teil, the best known lime of France, the lime of Pavier, known as of good quality, and upon limes of second grade coming from different factories of a particular province:

	Normal Test. 1st week.	3rd week.	6th week.	Swelling.	Test at 80°. 1st week. Strength. Kg.	Swelling.
	Kilograms.					
Lime of Teil	12.5	19.5	39	None	69.0	None
Lime of Pavier	3.6	6.5	17	None	48.0	None
1	19.5	33.0	51	Slight	30.0	15%
2	8.0	13.0	33	Slight	7.5	30%
3	16.5	21.0	27	Slight	15.0	30%

These numbers express the crushing strength per square centimeter of small cylinders 2 centimeters high and 2 centimeters in diameter.

We see from this table that the tests made in the cold give a great superiority to limes of inferior quality. This initial excess of strength results wholly from lack of slaking, that is, from careless manufacture. The hot tests, on the contrary, immediately place these different products in their respective places, and show, by a considerable swelling, the lack of slaking in the limes of second quality.

In order to make these tests, the briquettes are left to set for twenty-four hours at the ordinary temperature and are then immersed in a water bath heated to a temperature near to 100° C. It is necessary to avoid placing them in boiling water, which, by its agitation, would disintegrate those briquettes whose set is slow. The result obtained in this case would be more complex, being a function both of the quickness of the set and the final hardness. Slow setting limes, like those of Teil, would be completely disintegrated, whereas, very mediocre Roman cements would

resist this action. Forty-eight hours' heating in hot water seems to suffice for obtaining the larger part of the effects of swelling, and consequently, the integral disintegration which it is purposed to make evident. At the end of seven days the maximum strength seems to be reached.

These hot water tests might be completed by a desiccation at 100° C. in dry air, which brings about the destruction of the slightly stable hydrates. By this mode of comparison, we assign again to their true place certain products whose cold tests made at normal temperatures, and after too short a time after taking set, we might assign a different rank. Certain Roman cements, such as those of Vassy, the inferiority of which, as compared with Portland cement, no one doubts, may, however, occasionally give higher figures for tensile strengths in the tests made at one month. If, on the contrary, before breaking the briquettes they are put after desiccation into air heated at 100°, we see that the Roman cements lose half of their strength, whereas, the Portland cements are unchanged.

Test of the strength after seven days of setting:

Test of the strength after seven days of setting.

	Briquettes.	
	Not heated.	Heated to 100°.
Roman cement from Vassy.........	630,650,750	400,325,340
Cement from Teil.................	480	460,430
Portland cement..................	625	640

It seems to me that similar tests combined with measuring the quickness of the set, a fact equally useful to know, would allow the value of a cement to be judged much more exactly than the actual methods of testing do, but I am obliged to add immediately that my experiments upon this subject are not sufficiently numerous to allow, at present, the absolute accuracy of this mode of classification of hy-

draulic products to be affirmed. Numerous experiments ought still to be made before it could be accepted in practice. Therefore, no manner of testing exists meriting any confidence, the only means of judging of the quality of hydraulic materials is of assuring one's self of the identity of the product considered with a similar product having the same origin, and used successfully many years before.* From this particular point of view, the object of the tests ought to be merely that of establishing this identity: the results will be the more certain, as the identity of a greater number of different characteristics have been established: chemical composition, heat of solution, density, strength, &c. If it is desired to make a choice, it will be necessary

* This way of looking upon the tests by reducing them to a simple control of identification, is extremely hurtful to the progress of the industry of the hydraulic products: there is more and more a tendency at present, and with reason, to abandon this point of view. If still we have not succeeded in defining the tests of quality sufficient for an exact classification of all the hydraulic products, in view of all their applications, still some progress has been made in this direction.

The hot water or vapor tests give an absolute security against the presence of the expansives, lime or magnesia. (*H. Le Chatelier. Sur l'essai à chaud des produits hydrauliques, Bulletin de la Société d'encouragement pour l'industrie nationale, novembre, 1898*).

The mechanical 28-day tests give at least for Portland cements sufficient indications of quality, because with the fine grinding used at the present day, these cements have, after a month's set, almost the maximum strength. The same is true for slag cements. On the contrary, they are wholly insufficient for Roman cements, the cements from coarse powders and the hydraulic limes. For these two last classes of products the tests of hardening in boiling water would doubtless be employed very advantageously.

Still, the satisfactory test for controlling the resistance of a cement to the decomposing action of sea water does not exist. It seems, however, that a satisfactory solution will be reached shortly. Possibly it will be sufficient to mix the cement tested with a given quantity of gypsum, from 20 per cent. to 50 per cent., and to follow the decomposition of the briquettes, or their expansion measured with a rather precise apparatus, or yet their mechanical strength.

to try for characteristics which allow the greatest differentiations between similar products to be established, that is to say, to those which are susceptible of the greatest variations, and, at the same time, of the most precise measurement. It is not necessary from this particular point of view to apply ourself to the characters having any relation whatever with the necessary qualities for the use of a cement.

APPENDIX.

1 gram (g)=15.4322 grains.

1 kilogram (kg.) = 1000 grams = 2.2046 pounds.

To convert kilograms per square centimeter into pounds per square inch, multiply by 14.223.

To convert degrees Centigrade into degrees Fahrenheit,

$$\frac{9}{5}C^\circ + 32 = F^\circ.$$

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